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(54) Eingetrübte Kunststoffelemente

Die Erfindung betrifft eingetrübte Kunststoffelemente, enthaltend eine Polymermatrix in Anteilen von 3-30 Gew.-% bezogen auf die Polymermatrix und als teilchenförmiges Trübungsmittel, wobei die vernetzten Perlen aus einem Polymerisat bestehen, das

zu 9,9 bis 59,9 Gew.-% aus einem oder mehreren radikalisch polymerisierbaren Monomeren A, die einen aromatischen Rest enthalten oder nicht-aromatischen Monomeren A', die Halogen enthalten und

zu 90 bis 40 Gew.-% aus mit diesen Monomeren copolymerisierbaren, aber von diesen verschiedenen, vinylischen Monomeren B und

zu 0,1 bis 20 Gew.-% mindestens eines vernetzenden Monomeren V und

zu 0 bis 10 Gew.-% eines (stark) polaren Monomeren H aufgebaut ist, mit der Maßgabe, daß

a) der Brechungsindex des Polymerisats höher ist als der der Polymermatrix und daß

b) die mittlere Perlgröße der Perlen bei 20-50 μm liegt.

Patentansprüche

1. Eingetrübte Kunststoffelemente, enthaltend eine Polymermatrix und ein teilchenförmiges Trübungsmittel, dadurch gekennzeichnet, daß eine Polymermatrix (PM) in Anteilen von 3—30 Gew.-%, bezogen auf die Polymermatrix (PM), vernetzte Perlen enthält, wobei die vernetzten Perlen aus Polymerisat P bestehen, das
zu 9,9 bis 59,9 Gew.-% aus einem oder mehreren radikalisch polymerisierbaren Monomeren A, die einen aromatischen Rest enthalten oder nicht-aromatischen Monomeren A', die Halogen enthalten und
zu 90 bis 40 Gew.-% aus mit diesen Monomeren copolymerisierbaren, aber von diesen verschiedenen, vinylischen Monomeren B und
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zu 0 bis 10 Gew.-% eines (stark)polaren Monomeren H
aufgebaut ist, mit der Maßgabe, daß
   a) der Brechungsindex des Polymerisats P höher ist als der der Polymermatrix (PM) und daß
   b) die mittlere Perlgröße der Perlen bei 20—50 μm liegt.

2. Eingetrübte Kunststoffelemente gemäß Anspruch 1 dadurch gekennzeichnet, daß sie durch Zudosierung der vernetzten Perlen in der Schmelze der Polymermatrix PM im Zuge eines Extrusionsverfahrens hergestellt worden sind.

Beschreibung

Gebiet der Erfindung

Die Erfindung betrifft eingetrübte Kunststoffelemente, insbesondere geformte und flächige Kunststoffelemente aus an sich transparenten Kunststoffen, die sich speziell als Licht-Projektionsschirme, z. B. als Fernsehprojektionsschirme eignen.

Stand der Technik

Verschiedene Aufgaben lassen sich technisch durch Anwendung nur teildurchlässiger Gläser lösen. Zu diesen Aufgaben gehört die Mattierung von Verglasungen ebenso wie die Herstellung von Projektionsschirmen und sonstigen optischen Darstellungselementen.

Man bedient sich in der Regel der Lichtbrechung bzw. Lichtstreuung an Phasengrenzen, wie sie z. B. auftritt, wenn Partikel geeigneter Abmessungen als disperse Phase in einer Trägerphase eingebettet sind und beide Phasen verschiedene Brechungsindices besitzen. Die Trägerphase besteht z. B. vorteilhaft aus Kunststoffen. Die Technik hat, neben anorganischen Partikeln wie z. B. Glaskugeln geeignete Polymerpartikel zur Einbettung in die Trägerphase entwickelt.

So ist z. B. aus der DE-OS 21 46 628 ein Polymerisationsverfahren zur Herstellung von feinteiligen Polymerpartikeln bekannt, wobei man in einem Monomerensystem (A), welches zur durch freie Radikale bewirkten Additionspolymerisation imstande ist und

87 bis 99,99 Gew.-% eines monoäthylenisch ungesättigten Monomeren und

0,01 bis 3 Gew.-% mindestens eines mehrfach ungesättigten Monomeren enthält,

5 bis 50 Gew.-%, bezogen auf die gesamte Mischung eines anderen löslichen thermoplastischen Additionspolymeren vollständig löst, und wobei das erstere Polymere in dem thermoplastischen Polymeren unlöslich ist; und die Lösung aus beiden Bedingungen unterwirft, bei denen das Monomersystem mittels freier Radikale unter Bildung von im wesentlichen sphärisch geformten vernetzten Polymerpartikeln polymerisiert, wobei die Teilchen eine durchschnittliche Teilchengröße im Bereich von 0,5 bis 30 μm aufweisen und in einer kontinuierlichen Phase des thermoplastischen Polymeren dispergiert sind.

Die Polymerpartikel gemäß der DE-OS sind vernetzt und daher kaum schmelz- und wenig verformbar, so daß sie z. B. mit Pulvern verpreßt oder dem Spritzgießverfahren unterworfen werden können.

In Form von Lösungen kann das Polymerisat z. B. auf Acrylharzplatten aufgesprüht werden. Erwähnt wird die Verwendbarkeit als Mattierungslack sowie als Gemische, die für die Herstellung von Sichtschirmen mit rückwärtiger Projektion geeignet sind und bei Computern, in der Fernseh- oder Filmindustrie, Photographie usw.

Aus der DE-OS 21 46 607 sind ferner durchscheinende bis opake Kunststoffgemische bekannt, die kugelförmige vernetzte Additionspolymerpartikel zu 87—99,99 Gew.-%, mindestens eines monoethylenisch ungesättigten Monomeren und 0,01 bis 3 Gew.-% eines monomeren Vernetzers dispergiert in einer kontinuierlichen Phase eines Additionspolymerisats, enthalten, wobei das Additionspolymerisat in den vermischten Monomeren löslich sein soll. Vorzugsweise enthält das Kunststoffgemisch noch zusätzliches, mischpolymerisiertes Vernetzungsmittel. Als Anwendungsgebiete werden selbsttragende, durchscheinende Kunststoffplatten, Folienbahnen u. a. angegeben. Durch Aufsprühen einer Lösung des polymeren Materials auf Acrylfolien erhält man mattierte Folien. Außerdem sollen sich die Gemische für Bildschirme mit rückwärtiger Projektion eignen.

Die JP-OS 80 93 102 (Chem. Abstr. 93, 240 792 y) beschreibt lichtstreuende Acrylharzplatten, die mittels Bandpolymerisation aus Acrylharzfilm und Acrylatmonomeren, die ein lichtstreuendes Mittel enthalten in Sandwichkonfiguration gewonnen werden.

Aus der JP-OS 81 117 225 (Chem. Abstr. 96, 86 627 b) sind optische Schirme bekannt, die in einer Richtung eine breite Lichtdiffusionswirkung und in der anderen Richtung die Wirkung optischer Linsen aufweisen.

Hergestellt werden sie durch Einbettung gepulverter Glasfasern in modifiziertem Acrylharz und anschließender einachsiger Reckung, gefolgt von einer Schlußbeschichtung mit einer rußhaltigen Acrylatschicht. Lichtstreuende Acrylharzscheiben als Projektionsschirme sind Gegenstand der JP-OS 82 05 742 (Chem. Abstr. 96,

200 748 a), wobei die gewünschte Lichtstreuung durch eingebettete Quarzkügelchen mit 0,5—20 µm Durchmesser in PMMA erreicht wird. Laut GB-PS 15 85 338 erhält man lichtstreuende Platten mit besserer optischer Auflösung, größerem optischen Halbwertswinkel und größerer Flexibilität als gewöhnliche glasfaserhaltige Platten, wenn man Kunststoffplatten verwendet, die mit Glaskugeln gefüllt sind. Die Glaskugeln haben Durchmesser von 0,001 bis 0,05 mm. Als Trägermaterialien werden Thermoplasten wie Celluloseester, Polycarbonat, Polyarylsulfon, Polystyrol oder Acrylharze genannt.

Aufgabe

Die Lösungen des Standes der Technik bezüglich "durchscheinende bis opake Kunststoffgemische und deren Verwendung z. B. zur Herstellung von Platten- oder Folienmaterial" konnten indessen nicht voll befriedigen. Insbesondere sind hinsichtlich der Eignung als optische Projektionsschirme die Ansprüche nicht voll befriedigt worden. Zu fordern was insbesondere auch die Extrudierbarkeit ohne einschneidende technische Nachteile.

Lösung

Es wurde nun gefunden, daß eingetrübte, insbesondere geformte flächige Kunststoffelemente die Anforderungen an optische Projektionsschirme, speziell Fernsehprojektionsschirme, in besonderem Maße erfüllen, wenn man einer Polymermatrix (PM) in Anteilen von 3—30 Gew.-%, bezogen auf die Polymermatrix (PM), vernetzte Perlen zusetzt, wobei die vernetzten Perlen aus Polymerisat P bestehen, das

zu 9,9 bis 59,9 Gew.-% aus einem oder mehreren radikalisch polymerisierbaren Monomeren A, die einen aromatischen Rest enthalten oder nicht-aromatischen Monomeren A', die Halogen enthalten und

zu 90 bis 40 Gew.-% aus mit diesem Monomeren copolymerisierbaren, aber von diesen verschiedenen, vinylischen Monomeren B und

zu 0,1 bis 20 Gew.-% mindestens eines vernetzenden Monomeren V und

zu 0 bis 10 Gew.-% eines (stark)polaren Monomeren H

aufgebaut ist, mit der Maßgabe, daß

a) der Brechungsindex des Polimerisats P höher ist als der der Polymermatrix, daß

b) die mittlere Perlgröße der Perlen bei 20—50 µm, vorzugsweise bei 20—35 µm liegt.

Unter den radikalisch polymerisierbaren Monomeren A, die einen aromatischen Rest enthalten seien Monomere der Formel I

$$Ar - \left[(O)_m - R'_p - O - \overset{O}{\underset{\|}{C}} - \right]_n - \overset{R}{\underset{|}{C}} = CH_2 \qquad (I)$$

worin Ar für einen gegebenenfalls substituierten aromatischen Kohlenwasserstoffrest mit bis zu 12 Kohlenstoffatomen, vorzugsweise einen gegebenenfalls mit C_1-C_4-Alkylresten oder mit Fluor, Chlor oder Brom oder beiden Substituententypen substituierten aromatischen Rest, insbesondere einen Phenylrest,

R für Wasserstoff oder Methyl

R' für einen gegebenenfalls verzweigten Alkylenrest mit 1 bis 8 Kohlenstoffatomen

n für null oder eins

m für null oder eins und

p für null oder eins mit der Maßgabe, daß wenn p für null steht, auch m für null stehen soll,

verstanden. Die nur aus Monomeren der Formel I gebildeten Homo- und Copolymerisate weisen in der Regel einen Brechungsindex N_d von > 1,56 auf.

Vorzugsweise handelt es sich bei den Monomeren der Formel I um Styrol und seine methylsubstituierten Derivate wie das α-Methyl- und das p-Methylstyrol, das p-Ethylstyrol, sowie halogenierte Derivate des Styrols wie das p-Chlorstyrol. Weiter kommen als Monomeren A der Formel I beispielsweise Phenylacrylat und -methacrylat, Xylylenmethacrylat und -acrylat, insbesondere die m-Form, 4-Methylphenylacrylat und -methacrylat, 2-Phenylethylacrylat und -methacrylat, 3-Phenyl-1-propylmethacrylat und -acrylat, 2-Phenyl-oxyethylacrylat und -methacrylat infrage.

Unter den nicht-aromatischen Monomeren A', die Halogen enthalten, seien solche verstanden, die insbesondere Chlor oder Brom in nicht aktivierter, demnach leicht hydrolisierbarer Bindung enthalten, beispielsweise die α-Chlor und α-Bromacryl- und -methacrylsäureester von C_1-C_4-Alkoholen wie z. B. der α-Chloracrylsäuremethylester, ferner Vinylchlorid und Vinylidenchlorid.

Unter den vinylisch copolymerisierbaren Monomeren B seien insbesondere solche der Formel II

$$CH = \overset{R}{\underset{|}{C}} - COOR'' \qquad (II)$$

worin R für Wasserstoff oder Methyl und R'' für einen gegebenenfalls verzweigten, gegebenenfalls cyclischen Alkylrest mit 1 bis 8 Kohlenstoffatomen, wobei die cyclischen Alkylreste vorzugsweise mindestens 5 Ringkohlenstoffatome besitzen. Von den Monomeren der Gruppen A, B und C können jeweils auch verschiedene Vertreter eingesetzt werden, soweit dies in der Wirkung den angegebenen Merkmalen entspricht. Die nur aus Monomeren der Formel II gebildeten Homo- und Copolymerisate weisen in der Regel einen Brechungsindex N_d

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von < 1,51 auf, im allgemeinen < 1,49.

Vorzugsweise werden die vinylischen Monomeren B so ausgewählt, daß die (dilatometrisch ermittelte) resultierende Glastemperatur T_g eines daraus hergestellten Polymeren bzw. Copolymeren mindestens 80° C betragen würde. (Zur T_g und den Beiträgen der Monomeren vgl. Brandrup-Immergut, und B. Vieweg, F. Esser, im Kunststoff-Handbuch, Bd. IX, Hanser-Verlag 1975, pp 333—340; T.G. Fox Bull. Am. Phys. Soc. 1, 125, 1956.)

Besonders bevorzugt besteht das vinylische Monomere B ganz oder zu mindestens 40 Gew.-% aus Methylmethacrylat.

Unter den vernetzenden Monomeren V, seien die an sich bekannten radikalischen Vernetzer verstanden. Die vernetzenden Monomeren besitzen üblicherweise mehr als eine radikalisch polymerisierbare Einheit im Molekül. Genannt seien solche mit zwei vinylischen Gruppen wie Divinylbenzol, ferner Acryl- und Methacrylsäureester und -amide von Polyolen wie Glykoldi(meth)acrylat, 1,3- und 1,4-Butandiol(meth)acrylat, Trimethylolpropantri(meth)-acrylat, Tetraäthylenglykoldi(meth)acrylat usw., weiter Monomere, die Vinyliden-, die (verkappte) Amidmethylol-, Carbamidmethyloläther-, Azlacton- und Epoxygruppen enthalten, wie N-Methylol(meth)acrylamid, Methylenbisacrylamid und methacrylamid, Glycidyl(meth)acrylat, insbesondere auch vernetzende Monomere mit ungesättigten Gruppen abgestufter Reaktivität im Molekül wie die Vinyl-, Allyl- und Crotylester der Acryl- und/oder Methacrylsäure. (Vgl. H. Rauch-Puntigam, Th. Völker, Acryl- und Methacrylverbindungen, Springer-Verlag Berlin, 1967.) Die Vernetzung soll u. a. bewirken, daß die Perlen bei der Verarbeitung bei erhöhter Temperatur (bis ca. 300° C) nicht aufschmelzen.

Zur Herstellung der Perlen

Die Perlpolymerisate werden in bekannter Weise nach den Verfahren der Perlpolymerisation hergestellt. Bei diesem Verfahren werden die Monomeren A, B und V als disperse Phase durch Einwirkung mechanischer Kräfte (Rührung) in einem Nichtlösungsmittel (kontinuierliche Phase) verteilt und in dieser Form polymerisiert. Das gebildete Polymerisat ist überwiegend im Monomeren löslich. Unter dem Einfluß der Grenzflächenspannung bildet das Monomere kugelförmige Tropfen. Um die Tropfenform während der Polymerisation zu erhalten und das Zusammenlaufen von Tropfen zu verhindern, setzt man dem Polymerisationsansatz sogenannte "Dispergatoren" oder Verteiler (Schutzkolloide) zu, vorzugsweise Substanzen, die sich nach beendeter Polymerisation vollständig von dem perlförmig anfallenden Polymerisat abtrennen lassen.

Der "Verteiler" bewirkt, daß die einmal gebildeten Monomertröpfchen soweit stabilisiert werden, daß eine Vereinigung von Tropfen praktisch unterbleibt.

Als kontinuierliche Phase verwendet man in der Regel Wasser. Als zur Polymerisation geeignete Monomere kommen daher primär schwerlösliche bis wasserunlösliche, radikalisch polymerisierbare Monomere in Frage. (Vgl. Houben-Weyl, 4. Auflage, Bd. XIV/1 "Makromolekulare Stoffe", S. 406—433, G. Thieme-Verlag 1961.)

Als Verteiler kommen (wasserunlösliche) Salze anorganischer Säuren, wie Bariumsulfat oder Bariumcarbonat oder hochmolekulare Naturstoffe oder synthetische Polymere in Frage. Zu der Gruppe der hochmolekularen Verteiler gehören wasserlösliche Kolloide, wie Polyvinylalkohol, teilweise verseiftes Polyvinylacetat, Methylcellulose, Stärke, Gelatine, Pektin, die Alkalisalze der Polyacrylsäure oder die Alkalisalze von Styrol- oder Vinylacetat-Maleinsäureanhydrid-copolymeren u. a. (Vgl. Houben-Weyl, loc.cit. S. 411—430.) Das Verhältnis der wäßrigen zur Monomerenphase liegt meist bei 2 : 1 bis 4 : 1. Bei der Perlpolymerisation werden bekanntlich Starter eingesetzt, die in erster Näherung im Monomeren löslich, aber in Wasser unlöslich sind. Meistens liegt die angewandte Startermenge bei 0,1 bis 1 Gew.-%, bevorzugt um 0,5 Gew.-%, bezogen auf die Monomeren. Als Starter kommen die üblichen in Monomeren löslichen organischen Peroxide oder entsprechende Azoverbindungen zur Anwendung, wie z. B. Dibenzoylperoxid, Lauroylperoxid, Azoisobutyronitril. Radikalbildner mit höheren Zerfallstemperaturen können zusätzlich verwendet werden, wenn gegen Reaktionsende zur möglichst vollständigen Polymerisation die Temperatur gesteigert wird. Die Perlgröße läßt sich in dem beanspruchten Rahmen zwischen 20 und 50 μm einstellen.

Ferner können dem Perlpolymerisationsansatz gegebenenfalls Regler, wie z. B. die üblichen Schwefelregler, z. B. aliphatische Mercaptane wie Laurylmercaptan, tert. Dodecylmercaptan zugesetzt werden. Das gewichtsmittlere Molekulargewicht M_w des erfindungsgemäß verwendeten Polymerisats P liegt im allgemeinen im Bereich von 1 bis 2 · 10⁵ g/Mol; als Richtwert sei ca. 10⁵ g/Mol angegeben (M_w ermittelt durch Gelpermeationschromatographie).

Ferner können die üblicherweise verwendeten Gleitmittel wie Fettalkohole, Stearinsäureester, Palmitinsäureester oder natürliche Wachse — vorzugsweise vor der Polymerisation — zugesetzt werden.

Die praktische Durchführung kann so erfolgen, daß das Wasser, die Monomeren A, B und V, Starter, Dispergiermittel und gegebenenfalls Gleitmittel zusammen vorgelegt und dann erhitzt werden, beispielsweise auf ca. 90° C. Gegebenenfalls wird die überschüssige Polymerisationswärme, besonders ab 95° C, durch äußere Kühlung abgeführt. Die Temperatur wird 115° C nicht übersteigen. Die Dauer der Polymerisation liegt im Bereich von 1 bis 5 Stunden. Die Viskosität des Polymerisationsansatzes (gemessen mit dem Brookfield-Viskosimeter) liegt im allgemeinen im Bereich zwischen 8000 und 800 mPa · s.

Die zum Teil reaktiven Gleitmittel werden vorzugsweise erst ab etwa 20% Umsatz zugesetzt. Auch der Zusatz von Reglern kann im Verlauf der Polymerisation erfolgen.

Nach Reaktionsende werden die Perlen im allgemeinen durch Filtration oder Zentrifugation abgetrennt. Anhaftende Zusätze können auf geeignete Weise, beispielsweise durch Waschen mit verdünnter Säure und Wasser entfernt werden. Die Perlen werden häufig unter Erwärmen, vorzugsweise mit Luftumwälzung, getrocknet, z. B. in Hordenschränken.

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Die Polymermatrix *PM*

Bei der Polymermatrix *PM*, welcher die Perlen zugesetzt werden, handelt es sich um, in der Regel transparente, im allgemeinen thermoplastische Kunststoffe, wie sie zum Zweck der Lichtprojektion bereits Eingang in die Technik gefunden haben.

Das Verhältnis zwischen *P* und *PM* wird u. a. dadurch bestimmt, daß die Differenz der Brechungsindices n_D Perle minus n_D Polymermatrix mindestens den Wert 0,02, vorzugsweise 0,04 haben soll.

Als geeignete Kunststoffe für die Polymermatrix kommen Polystyrole, PVC, Polyvinylacetat, Polycarbonat, Polyolefine und insbesondere Acrylharze in Frage.

Unter Acrylharzen im Sinne der vorliegenden Erfindung seien Polymerisate verstanden, die zu mindestens 50 Gew.-% aus monomeren Estern der Acryl- und/oder der Methacrylsäure, insbesondere der vom Typ der Formel II aufgebaut sind.

Zur Herstellung der erfindungsgemäßen eingetrübten Kunststoffelemente müssen die aus dem Polymerisat *P* bestehenden Perlen in die Polymermatrix eingebracht und dann verteilt werden.

Als besonders überraschend muß betrachtet werden, daß es gelingt, im Zuge der Verarbeitung der Polymermatrix *PM* mit Hilfe von Extrudern die Perlen einzubringen. Dabei werden die Perlen in die Extruderschmelze eingetragen.

Es war nicht zu erwarten, daß a) die Perlen unter den Temperatur- und Scherbedingungen einer Extrusion ihre Gestalt beibehalten würden und b) daß die zur angestrebten Lichtstreuwirkung unbedingt notwendige homogene Verteilung der Perlen erzielbar sei. Darüber hinaus wurde überraschenderweise der ebenfalls für die erforderliche Lichtstreuwirkung notwendige Sprung der Brechzahl an den Grenzflächen zwischen der Polymermatrix *PM* und den Polymerisatperlen erzielt. Es stand zu befürchten, daß dieser Sprung im Verlauf der Brechzahl an den o. g. Grenzflächen durch Diffusionsvorgänge "eingeebnet" würde — wie es z. B. beim Einbringen der Perlen in polymerisierbare Monomere geschieht — was in einer unerwünschten Veränderung der Streuwirkung resultieren würde.

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HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS, AND
TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

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VOLUME XXIX

POLYMERIZATION PROCESSES

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v

TABLE 5.1

Polymerization Processes in Heterogeneous Aqueous Dispersions

Process	Monomers	In aqueous phase	Initiator	Type of polymer product	Examples of commercial polymers and copolymers
Emulsion polymerization	Largely water insoluble	Initiators, emulsifiers, etc., e.g., persulfates, redox systems	Water soluble,	Latex of particles, 0.05–0.2 microns	Methacrylate and acrylate esters, vinyl acetate, styrene, butadiene
"Dispersion polymerization"	Largely water insoluble	Initiator and < 1 % water-soluble polymeric dispersant, e.g., PVA	Water soluble, e.g., H_2O_2	Viscous, latexlike dispersions, 0.5–10 microns	Vinyl acetate
Bead-type suspension polymerization"	Largely water insoluble	< 1 % water-soluble polymer or inorganic suspending agents	Monomer-soluble peroxides or azo compounds	Clear beads	Styrene, meth-acrylate, acrylate, vinyl acetate
Powder-type suspension polymerization"	Polymer insoluble in monomer	With or without suspending agents	Monomer-soluble peroxides or azo compounds	Opaque pearls or powders	Vinyl chloride, high-acrylonitrile, fluoroethylene

"Cf. Ullmann, Encycl. Tech. Chem., 3rd ed., 14, 123 (1963).

5. POLYMERIZATIONS IN SUSPENSION

MANFRED MUNZER AND ERNST TROMMSDORFF, Research Laboratories, ROEHM G.M.B.H., Darmstadt, Germany

Polymerizations in aqueous suspensions were reviewed in 1956 (1). This chapter emphasizes later developments and includes some different points of view. Polymerizations in heterogeneous systems offer many advantages that have led to their wide use in commercial production. Processes carried out in aqueous dispersion have by far the greatest importance, but recently dispersions in organic media have become practical. Important types of dispersions for polymerization are outlined in Table 5.1. Emulsion polymerizations and related dispersion polymerizations have special value in forming finely divided, stable, latexlike dispersions useful directly for coatings, adhesives, etc., but are less suitable for preparing polymers of high purity free of emulsifiers, coagulating agents, and catalyst residues. In contrast, suspension or bead polymerizations give relatively large particles of better purity which are simply isolated; e.g., directly by centrifuging or filtering. These suspension polymers find wide application in molding plastics, ion exchange resins, and as flocculating agents.

In typical suspension systems one or more water-immiscible liquid monomers containing polymerization initiator are dispersed into droplets by strong stirring, and suitable conditions of mechanical agitation are maintained while polymerization is completed to solid beads or pearls. The dissipation of the considerable heat evolved in addition polymerizations, often the major problem when carried out in bulk without solvents or dispersing liquids, is facilitated by the water phase of high specific heat and low viscosity. An example is the polymerization of methyl methacrylate (MMA) by equation shown on page 37.

With few exceptions suspension polymerizations in water require small amounts of substances that hinder the coalescence of monomer droplets and sticking together of beads during the course of polymerization. They are generally called suspension stabilizers or suspending agents. The solid polymer may be obtained in the same spherical form in which the monomer was dispersed in the aqueous phase. Particle size can be controlled by the agitation to give beads in sizes that can be easily separated from water. If the monomer is a solvent for the polymer a viscous syrupy stage is passed through

to form clear little spheres. See Fig. 5.1. If the monomer does not dissolve the polymer then a bulk, precipitation polymerization occurs in each drop and
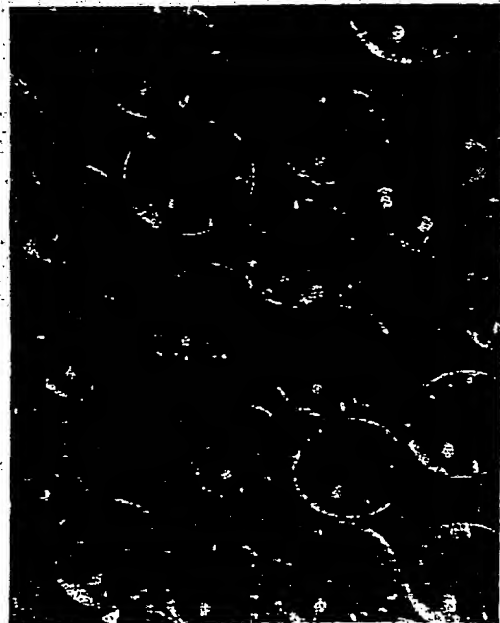

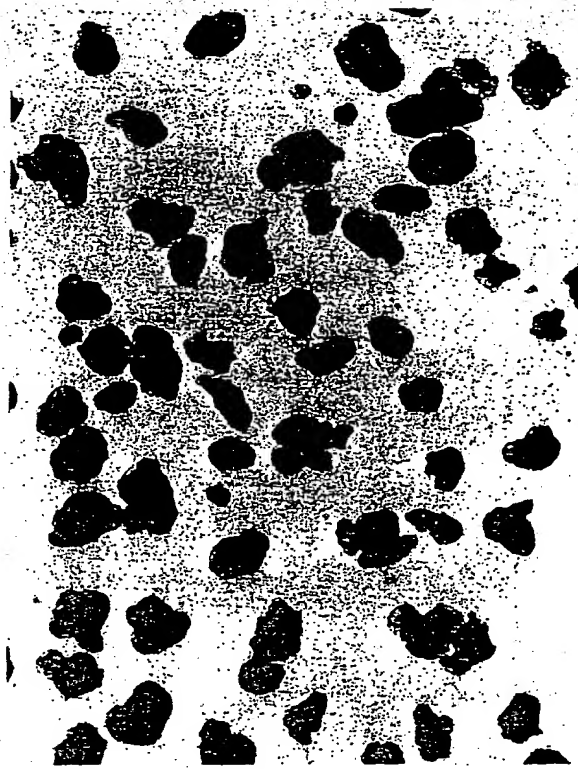Fig. 5.1. Beads of MMA polymer from suspension polymerization (× 100). Roehm G.m.b.H., Darmstadt.

Fig. 5.2. Polyvinyl chloride particles from suspension polymerization (× 50). BASF, Ludwigshafen.

opaque, irregular grains or powders often are formed (2). See Fig. 5.2. One may distinguish this between bead suspension and powder suspension polymerizations.

Other polymerizations in heterogeneous aqueous media may be carried out to give different products, for example, so-called aqueous dispersion polymerizations or projective colloid-emulsion polymerizations of vinyl acetate. These are distinguished from suspension polymerizations by the use of relatively large amounts of water-soluble polymeric dispersant ("protective colloid" such as polyvinyl alcohol) and by initiation in aqueous phase, and from typical emulsion polymerizations in giving more coarse, viscous dispersions having particle sizes 0.5–10 microns (1). Such vinyl acetate polymer dispersions much used as adhesives are relatively stable on storage. They often show graft polymerization with the dispersing agent, which may be partially insolubilized. These systems are closely related to emulsion polymerizations.

The principles of suspension polymerization have been extended to reverse bead polymerization for manufacture of water-soluble polymers such as acrylamide copolymers. The monomers alone or in concentrated aqueous solution are dispersed with agitation as droplets in an immiscible organic solvent and then polymerized. These should not be called reversible emulsion polymerizations since they seldom form typical, stable latices. Polymerization processes that begin with homogeneous solutions from which granular polymers are formed as suspensions have been called "dispersion polymerizations in organic phase"; conditions for forming bead polymers from such systems have been developed recently.

I. HISTORICAL

Bead-type suspension polymerization was developed to meet manufacturing needs. Large-scaled bulk or mass polymerizations of active monomers such as acrylic and methacrylic esters without a diluent are very difficult to control because of the heat of polymerization evolved. Except in thin layers or by very slow cast polymerizations, heat cannot be removed to obtain reproducible products with more than 100 g of monomer. In emulsion polymerization water serves well as a heat exchange agent, but the polymers obtained after coagulation of the latex are contaminated by impurities such as emulsifier residues which impair their usefulness. Bauer and Lauth dispersed acrylic esters in water or electrolyte solution and removed the heat of polymerization through the agitated aqueous phase (3). The polymer formed as spheres of size depending upon the intensity of stirring. This early process was limited in utility by the tendency for agglomeration or clumping of the adhesive, partially polymerized particles. The first bead polymer available

commercially was vinyl chloroacetate polymer (Mowolith G) supplied as clear spheres of 0.5–1.0 mm diameter which were readily soluble in solvents for use in lacquers (4). The polymerizations were carried out in aqueous electrolyte solution with addition of soaplike emulsifiers under conditions that finely divided emulsion and latex particles did not form. This process also could be used with other vinyl esters, but it did not become commercially important.

Substantial progress in the art and application of suspension polymerizations followed the introduction of suspending agents or suspension stabilizers (also known in England as granulating agents aid in Germany as Verteiler). Crawford of Imperial Chemical Industries developed processes using water-soluble high polymeric suspending agents especially for production of clear methyl methacrylate polymer beads (5). Roehm and Trommsdorff discovered that certain water-insoluble, finely divided powders are useful as suspending agents (6). These processes were much further developed during the last 40 yr, and they form today the basis for commercial preparation of polymers from many monomers, among the most important being acrylic esters, methacrylic esters, styrene, vinyl acetate, vinyl chloride, and these with monofunctional or polyfunctional comonomers. Suspension polymerization has found little application with ionic and with condensation polymerizations (7).

From the work of Trommsdorff and co-workers (8), as well as Mark and Hohenstein (9), one concludes that ideal bead-type suspension polymerizations consist essentially of water-cooled bulk or mass polymerizations. The complex mechanisms and principles by which suspending agents operate have received qualitative clarification (10, 11). Much industrial art and numerous suggestions are found in the extensive patent literature.

II. MONOMER PHASE

The dispersed monomer phase in bead suspension polymerization contains initiators, regulators, and any other agents necessary for preparing polymer products suitable for specific applications. The monomer or monomer mixtures must be sufficiently insoluble in water to form a second phase. In contrast to bead polymerizations in the strict sense, suspension polymerizations of vinyl chloride, vinylidene chloride, and tetrafluoroethylene can be carried out in some cases without added suspending agents (12). For a range of important crosslinked bead polymers, such as styrene-based ion exchange resins, minor proportions of comonomers such as divinylbenzene, divinyl sulfone, polyfunctional acrylate, or methacrylate monomers may be added, or in other cases vinyl or allyl esters of unsaturated acids.

Monomers with considerable solubility in water such as acrylonitrile (13)

or methacrylic acid may be copolymerized with acrylic or methacrylic esters or styrene. This is possible because during the polymerization the water miscible monomer may diffuse into the organic phase for copolymerization. Such processes may be promoted by additions of certain water-insoluble solvents that act as extraction agents. Thus an addition of o-cresyl ethyl ether was recommended in suspension copolymerization of ethyl acrylate with acrylonitrile (14). In cases where there is a high proportion of water-soluble reactants, electrolytes have been added for a salting-out effect (15). Thus in the polymerization of methacrylic acid with methacrylate ester and styrene, presence of sodium sulfate or chloride can promote formation of hydrophilic beads. If the polymer formed is too water soluble, as in the case of acrylic acid and acrylamide, aqueous suspension polymerization is not possible but reverse suspension methods may be used.

Difference of solubilities of monomers being copolymerized in the two phases and the reactivity ratios must be considered in preparing homogeneous copolymers. The faster reacting monomer may be added gradually. For example, for preparation of a copolymer of vinyl chloride–vinylidene chloride (75:25) one may begin with a weight ratio 85:15 of monomers and gradually add more vinylidene chloride according to the pressure in the reactor (16). Rates of comonomer addition can control mechanical and rheological properties as in the case of vinyl chloride–octyl acrylate copolymers (17).

Most monomers are suspension polymerized as liquids. Vinyl chloride, normally a gas, is liquid under the pressures used in commerical suspension polymerizations. A few normally crystalline monomers such as N-vinylcarbazole may be suspension polymerized while melted. The monomers and agents used in suspension systems must have high purity. That molecular oxygen normally acts as an inhibitor of addition polymerization must be considered.

It is often practical to use the same polymerization initiators and regulators in aqueous suspension polymerizations as in bulk and solution polymerization of ethylenic monomers. They are generally dissolved directly in the monomer phase just before dispersion in water in order to avoid premature polymerization. The type and concentrations of initiators and regulators greatly affect the rates of polymerization and the properties of the products as discussed later in relation to kinetics. Other additions to the monomer phase may include foaming agents, such as butane and hexane, e.g., in styrene polymerization under pressure (18). Blowing agents may be present in polystyrene in the form of tiny occluded droplets (Fig. 5.3). MMA and comonomers may also give beads enclosing blowing agents (19). Styrene–divinylbenzene crosslinked beads are made for use in ion exchange. They have large internal surface resulting from added solvents or swelling agents that are removed after the suspension copolymerization (20). Good solvents for
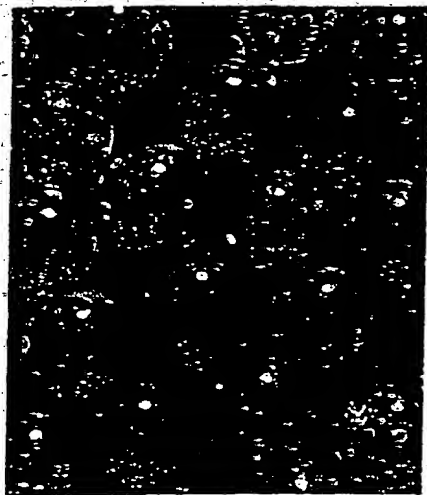
Fig. 5.3. Polystyrene beads containing pentane as blowing agent used for making foamed plastics (× 30). BASF, Ludwigshafen.

polystyrene such as toluene and xylene permit beads of 11% divinylbenzene units with styrene that do not collapse after removal of these solvents. If organic liquids are added that are only swelling agents for polystyrene then pearls of low divinylbenzene content having macroreticular crosslinked structure are obtained. These are different from particles obtained through use of more active aromatic solvents. Such pearls possess desirable inner surface and are not broken by osmotic forces during sulfonation (21).

Similarly, insoluble hydrophilic bead polymers with large inner surface can be prepared (146). For example, to ethylene glycol monomethacrylate may be added 10% ethylene glycol dimethacrylate and about 50% toluene and the mixture suspension copolymerized in water in presence of finely divided magnesium hydroxide. Macroporous, water-swollen beads or pearls are formed.

Dyestuffs and pigments are seldom added initially before suspension processes because of adverse effects upon the polymerization reactions. However, under special conditions coloring materials may be incorporated, especially if partially polymerized syrups are submitted to suspension polymerization (22). Other agents that are often added in small amounts to the monomer phase include UV-stabilizers such as aromatic ketones or esters, heat stabilizers, for example ethylene oxide derivatives, tin, lead, or barium compounds to vinyl chloride, and molding lubricants such as cetyl alcohol and stearic acid to methacrylate monomers. Acidic agents may interfere with the suspension process by promoting foam and reducing the efficiency. For this reason lubricants may be added near the thermal peak of polymerization, e.g., from

aqueous dispersion (23). The lubricant then is taken up at the surface of the beads. Such agents, as well as dyestuffs, more often are incorporated after polymerization in mixers or extruders while heating.

A. Kinetics

Early kinetic studies of suspension polymerizations were carried out with MMA and with styrene (8,9). Conversion and viscosity measurements were made after different times of reaction. The results indicated that bead polymerizations normally consist of water-cooled bulk polymerizations in monomer droplets. There was good agreement with bulk polymerization in time-conversion curves, heat of polymerization, and dependence of initial rate of polymerization upon initiator concentration. In general the rates of suspension polymerization were not much influenced by bead size and the type of suspending agent. More recently these conclusions have been confirmed by dilatometer studies of suspension polymerization of MMA (24). The polymerization kinetics of vinyl chloride polymerization in bulk and in suspension are similar (25).

The good agreement in kinetics between bulk polymerization and bead polymerization and the differences from emulsion polymerization can be interpreted by statistical methods. In emulsion polymerization only one growing chain radical may be detected in each micelle. In an MMA droplet (0.1 mm diameter with 0.2% AIBN as initiator at 75°C) in a stationary state there should be about 6×10^7 radicals. One monomer droplet thus is large enough for statistical consideration of chain growth and termination. In suspension polymerizations the influence of initiators and regulators correspond to those found in bulk polymerizations as long as these are soluble exclusively in the monomer phase.

The progress of a bead polymerization of MMA is similar to that of a well-cooled bulk polymerization. In the presence of molecular oxygen there is first an inhibition period, proportional to the oxygen concentration and related also to the inhibitor and initiator concentrations. The polymer peroxide formed may decompose into initiating radicals, also promoting polymerization. After the inhibition period there may result a period of fairly constant reaction speed that transforms into an accelerating rate of polymerization due to the gel or Trommsdorff effect. The onset of the latter occurs with increase in viscosity and also depends upon conversion as shown in Fig. 5.4. The chain termination rate by reaction of growing chains becomes diffusion controlled and, therefore, slower than the rates of chain growth. The gel effect leads to distinctly higher molecular weights and wider molecular weight distributions than formed at low conversion. In a later stage of the polymerization the rate falls off because of exhaustion of the free mono-
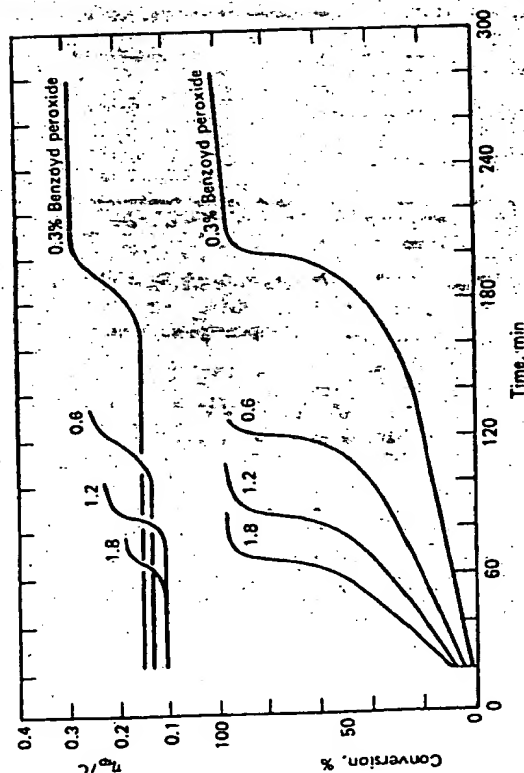
5.4. Suspension polymerization of methyl methacrylate at 70–73°C (8). Above is given the variation with time of reaction of η_{sp}/C of the polymer formed and below is given the conversion with time. Rapid rise in rate and in polymer molecular weight occur with onset of the gel effect.

mer and onset of diffusion control of the growth reaction until polymerization finally ceases. Assuming sufficient initiating radicals are present, these final phenomena are influenced by the temperature of polymerization and the glass temperature of the polymer.

The correspondence between bulk and suspension polymerization is not complete. There can be differences, for example, when relatively water-soluble comonomers or auxiliary agents are present. The concentrations of reactive components at the locus of polymerization in the droplets depend upon the monomer distribution between the two liquid phases. Thereby significant differences in reactivity can occur, for example, by dipole–dipole interaction with water molecules. Thus the parameters for MMA copolymerization with methacrylic acid may be shifted from $r_1 = 0.35$ and $r_2 = 1.63$ in bulk copolymerization to $r_1 = 0.63$ and $r_2 = 0.07$ in suspension polymerization (26). Similar differences were observed for copolymerizations of methyl acrylate with the relatively water-soluble monomer acrylonitrile (27).

As polymerization progresses the dispersed phase becomes low in monomer, and in order to maintain the distribution equilibrium a back-diffusion of monomer out of the water phase may occur. Also the concentration of amphoteric molecules in the phase boundaries must not be neglected. Such effects can lead to inhomogeneity in polymer beads. Similar relationships are

met if one adds regulators of molecular weight having appreciable water solubility, such as thioglycol or thioglycolic acid. In some suspension polymerizations these are added also to reduce the molecular weight of a small fraction of polymer that may be formed by emulsion polymerization in the aqueous phase.

Bead polymerizations with water-miscible initiators are most practical and straightforward using highly water insoluble monomers such as styrenes and vinyl chloride. Otherwise too much polymer may be formed by emulsion and solution polymerizations in the water phase. Such undesirable fractions of different molecular weight and structure may be minimized by adding electrolytes to the aqueous phase to reduce solubility of the organic reactants or by adding small amounts of water-soluble inhibitors such as thiosulfates or thiocyanates.

The interchange of monomer between phases depends not only upon the distribution equilibria but also upon rates of reaching equilibrium. The latter depend upon the extent of boundary surfaces, which are related to the type and amounts of suspending agent. Also the rate of agitation apparently can influence polymerization kinetics at least in the case of suspension polymerization of vinyl acetate (28).

III. THE AQUEOUS PHASE AND SUSPENDING AGENTS

A. Mechanism of Bead Formation

Through the shearing action from the agitation and local turbulence, together with surface tension forces, the monomer assumes more or less stable spherical form. The weight ratio between monomer phase and water generally ranges from 50:50 to 25:75. Lower ratios are not limited but are seldom practical for economical production. Use of higher ratios is excluded by the proportion of water being insufficient to fill the volume between the monomer droplets. By extremely broad distribution of droplet sizes in certain emulsions the 1:1 ratio may be exceeded, but not in suspension polymerizations (29). Generally, particle size decreases with increasing rate of agitation in a given system. The equilibrium distribution of droplet size was reported to obey a Gaussian distribution (30).

Since the distribution of shearing action in an agitated reactor can be very nonuniform, an equilibrium condition is only possible if all the particles move through a zone of maximum shear. The time necessary for equilibrium increases with the viscosity of the dispersing phase, with decreasing droplet size, and with decreasing rate of agitation (29). The overturning action resulting from stirring must be strong enough that loss of the dispersion through settling and difference in density is hindered. The intensity of stirring normally is limited by the desired size of dispersed monomer droplets.

In such suspension systems the dispersed monomer droplets tend to run together, the number of collisions often depending upon the monomer–water ratio and the type of stirring. In practice apparently more than one collision occurs per second. On collisions the spherical shape is more or less strongly deformed. Such deformations increase with droplet size and with lowering of surface tension (31). The elastic deformation that occurs on most of the collisions, in combination with the liquid film of the continuous phase, produces a recoil of the droplets. On some of the collisions, however, the resulting deformations may produce a greater surface disturbance leading to a fusion of droplets. The following experiment shows that in such a system the monomer droplets are in dynamic equilibrium. If one colors a part of the monomer droplets with a water-insoluble dye and stirs, all the droplets are after some time equally colored. This shows continuous coalescence and redispersion.

If one carries out suspension polymerization under constant conditions of agitation without added dispersing agent, the viscosity of the droplets increases with conversion, the tendency for coalescence decreases, but redispersion also decreases, so that drop size increases and finally clumping may occur (before conversion and viscosity are high enough to prevent union of particles). For these reasons suspension polymerizations without special suspending agents are seldom sufficiently reproducible for commercial production. In the patent literature some suspension polymerizations such as those of lower acrylic esters have been described using only salt addition for modifying surface tension (32). In other cases impurities or side reactions may produce substances having dispersing action (33).

Suspending agents (Verteiler or granulating agents) that hinder coalescence in suspension polymerizations are of two types: (a) water-soluble organic polymers often called protective colloids and (b) finely divided, insoluble inorganic materials. Such suspending agents are only effective when present in the surface layers between the water and the monomer droplets. This must be emphasized in their choice and modification. Collisions of droplets enclosed by water layers containing such suspending agents less often result in coalescence than collisions in the absence of such the protective agents.

The mechanism of action of so-called "protective colloids" was studied by interferometer measurements of the liquid layers between styrene droplets (34). According to these studies the viscosity in the phase boundary layers is much higher in presence of added dispersing agent. The thickness of the liquid lamellae between the monomer droplets depending upon the type of suspending system was 60–2000 nm. The soluble suspending agent may form a gellike protective layer that keeps monomer droplets separated and hinders coalescence.

Although corresponding research on insoluble suspending agents has not been reported, one presumes that primarily these also hinder the approach

of monomer droplets. The tests of Mark and Hohenstein in presence of insoluble suspending agents established for a given system a "particle identity point"; that is, a degree of conversion at which no more coalescence occurs and from which particle size remains the same until the end of the polymerization reaction. No further interchange of dyestuff between particles should then occur. Merz found for bead polymerization of styrene a particle identity point at 50% conversion (35). Cf. ref. 36.

Wenning studied relations of suspending agent concentration with droplet size of styrene (29). For droplets of 0.35–0.90 mm he reported particle identity points between 3 and 40% conversion. The higher values for larger dispersed particles can be attributed to higher kinetic energy, which may shift the dynamic equilibrium to higher viscosity and to higher conversion. The use of smaller amounts of suspending agent also can lead to change of particle identity points. Wenning demonstrated that avoidance of coalescence results from complete covering of the droplet surface with suspending agent. The determination of bead size upon rates of stirring depends upon the presence of sufficient suspending agent. On the other hand, the dynamic equilibrium between coalescence and dispersion becomes more difficult as viscosity of the dispersed phase increases with polymerization. Finally, with increasing particle size the total surface can be covered by the suspending agent. The stabilizing action of suspension systems could be determined experimentally from the bead surface (37). Theoretical studies of liquid–liquid dispersions support the idea that bead size can be controlled by rates of agitation only within a limited range (38). For the relation of rates of agitation to bead size the following conclusions seemed to be valid:

1. Minimum bead size results from redispersion by agitation of the droplets that have coalesced.

2. The maximum bead size is limited by the shearing forces from agitation of the system.

3. The rate of agitation must be sufficient to hinder the blending tendency, which increases with drop size (depending upon the difference in densities of the two phases).

Three equations were proposed which by a log–log plot of particle size and rate of stirring predicted an area of stable dispersion. Of course many other factors influence stability of suspensions, such as density, viscosity, surface tension, thickness and properties of surface films.

B. Water-Soluble Suspending Agents

The first wide commercial use of suspension polymerization employed as suspending agents hydrophilic polymers or so-called protective colloids. Crawford in 1933 first developed bead polymerizations of MMA stabilized

initially by gelatin, tragacanth, or methyl cellulose. Natural water-soluble polymers soon were succeeded by synthetic dispersing polymers. Two of the most useful dispersing agents in commercial production have been partially saponified polyvinyl acetates (more often called polyvinyl alcohols) and alkali salts of methacrylic acid copolymers (5). The relations of the structure of these polymers to their effectiveness as suspending agents have been studied (29). The addition of soluble phosphate buffers may be critical in MMA suspension polymerizations (30).

Much of the research on polyvinyl alcohols as dispersing agents used relatively high concentrations leading to fairly stable polymer dispersions with properties closer to those of latices rather than bead polymers. Especially, 88% saponified polyvinyl acetate in the range of 1% in aqueous solution is used for the commercial so-called polyvinyl acetate emulsions. (1, 40). Such polymerizations do not give easily separated polymer particles. However, much smaller concentration of polyvinyl alcohols do find use for typical suspension polymerizations, for example, with vinyl chloride.

Hopff and co-workers showed that bead size may be proportional to prevailing boundary surface tension at the beginning of the reaction (41). The addition of very small amounts of so-called micellar colloids to lower surface tension in suspension polymerizations was disclosed in patents (42). However, larger additions of surface active agents prevent formation of polymer beads by leading to emulsion polymerization and latex formation (43).

Although precise investigations of the oriented adsorption at boundary surfaces are not available it is presumed that such adsorption occurs; for example, the ester groups of partially hydrolyzed polyvinyl acetate attracted to the monomer phase and the OH groups directed to the water phase. In accordance with experiments the molecular weight of dispersing agent has less influence than the number and length of the hydrophobic segments and the degree of hydrolysis. Therefore, protective polymers with a definite ratio between hydrophilic and hydrophobic groups often offer the best dispersing action. From the dependence of boundary surface tension upon concentration of protective colloids it was concluded that emulsifying effect results even from a monomolecular covering of the boundary surfaces (44). By use of different water-soluble organic agents dispersions intermediate in particle size between latices and bead polymers can be prepared. These may be regarded as emulsion polymers formed by diffusion of monomer and initiator into micelles of protective colloids rather than fine suspension polymerizations.

The intensive search for the best hydrophilic polymeric suspending agents for different monomers and different conditions of polymerization, at the same time keeping emulsion polymerization to a minimum and giving easily

TABLE 5.2

Hydrophilic Organic Suspending Agents

Natural polymers:

Starches, tragacanth, agar	
Pectins, plant gums, alginates	
Gelatins, fish protein	
Gelatin and monoethers of glycerol	J. W. C. Crawford et. al., Brit. 427,494 (ICI)
	Crawford, U.S. 2,194,354 (ICI)
	M. Lederer et al., Ger. 1,073,743 (Hoechst)

Modified natural polymers:

Methyl cellulose	Crawford, Brit. 427,494 (ICI)
Above and alkylaryl sulfonate	R. Dell, U.S. 3,004,009 (Allied)
Hydroxypropyl cellulose	J. L. Schick, U.S. 2,538,051 (Dow)
Hydroxyethyl cellulose	J. F. Corwin, Brit. 658,426 (Borden)
Carboxymethyl cellulose (Na salt)	G. Kraenzlein, Ger. 751,602 (IG)
Methyl ethers of polysaccharides	M. Naps, U.S. 2,494,517 (Shell)

Synthetic polymers:

Polymethacrylic acid plus buffer	
Methacrylic acid-2-ethylhexyl methacrylate copol.	D. Strain, U.S. 2,133,257 (DuPont)
	J. B. Ott, U.S. 2,862,912 (Monsanto)
Maleic anhydride-styrene copol.	C. A. Vana, U.S. 2,430,313 (DuPont)
Maleic anhydride-ethylene copol.	R. J. Longley, U.S. 2,823,200 (Monsanto)
Maleic anhydride-vinyl methyl ether copol.	M. Baer, U.S. 2,470,911 (Monsanto)
Copol. of fumaric, maleic and other unsaturated acids (also salts and partial esters)	Fr. 867,465 (Thomson-Houston)
Protective colloid + cationic dispersing agent	H. C. Hamann, U.S. 3,728,318 (R & H)
Partially saponified polyvinyl esters (PVA or vinyl alcohol-vinyl acetate copol.)	H. Berg, U.S. 2,279,436 (Chem. Forschung.)
PVA-styrene graft copol.	
Allyl alcohol-vinyl acetate copol.	D. Maragliano, Brit. 816,579 (Monte)
Polyvinyl pyrrolidone	G. Gatte, U.S. 3,228,919 (Edison)
Vinyl pyrrolidone-methyl acrylate copol. + Na alkylsulfate	H. Fikentscher, Ger. 801,233 (BASF)
Methacrylamide polymer + buffer	K. Wilkinson, Brit. 1,095,410 (Monsanto)
Methacrylamide polymerized *in situ*	W. E. Gordon, U.S. 2,067,234 (DuPont)
Polyvinyl pyridine	A. R. Ingram, U.S. 3,243,419 (Koppers)
Sulfonated polystyrene	W. Gumlich, Ger. 693,098 (IG)
Polyvinyl imidazoline salts	J. L. Schick, U.S. 2,538,050 (Dow)
Reaction products of PVA + aldehyde sulfonic acid	H. C. Hamann, U.S. 3,557,061 (R & H)
Phosphorylated PVA	W. Starck, Ger. 849,006 (Hoechst)
Vinyl ether polymers	H. Bauer, Ger. 1,062,009 (Wacker)
	R. G. Heiligmann, U.S. 2,886,552 (Diamond Alkali)
Ethylene oxide polymers	A. H. Turner, Brit. 873,948 (Shell)
Vinyl acetate-lactone copol.	R. E. Bingham, Fr. 1,265,742 (General Tire)

+ oxyethylated alkylphenol

TABLE 5.2 (Continued)

Urea–formaldehyde condensates	C. A. Brighton, U.S. 2,543,094 (Distillers)
Phenol–formaldehyde condensats	R. J. Wolf, U.S. 2,564,291 (Goodrich)
Agents of lower molecular weight	
Esters of hydroxy acids (e.g., octyl lactate)	A. Jahn, Ger. 878,863 (Hoechst)
Esters of phthalic acid	G. Bier, Ger. 888,172 (Hoechst)
Partial esters of polyols (e.g., pentaerythritol laurate)	Brit. 640,120 (Distillers)
Esters of polyethylene glycol	T. Boyd, U.S. 2,580,277 (Monsanto)
Polyglycol ethers	A. Jahn, Ger. 883,351 (Hoechst)

separated polymer beads, has resulted in a large patent literature. Besides natural and synthetic water-dispersible polymers and derivatives of the latter, many mixtures have been evaluated as well additions of very small amounts of true surface active or soaplike micelle-forming agents. In spite of a large literature, many parameters are insufficiently disclosed and much additional research could be done. A list of useful classes of suspending agents is given in Table 5.2; it makes no claim to completeness.

C. Insoluble Suspending Agents

Besides the water-soluble polymeric suspending agents the most important other group of stabilizing agents for suspension polymerization consist of insoluble powders most of which are inorganic. One of the outstanding commercial examples is the use of hydroxyapatite for suspension polymerization of styrene to commercial beads. Pickering showed long ago the use of inorganic dispersants in preparing emulsions from oils and water (45). Bechhold and co-workers showed improvement in emulsifying action by inorganic agents, as well as in reversed emulsions (46). In 1933 Roehm and Trommsdorff disclosed the first successful bead polymerizations using finely divided barium sulfate, talc, or aluminum hydroxide as suspending agents (6). Hohenstein and Mark (9) in bead polymerization of styrene used fine calcium phosphate (first discovered through its presence in table salt). Grim developed the use of hydroxyapatite along with controlled small concentrations of soaps or other surfactants (47). These systems, or with further additions, have been widely used industrially for bead polymerization of styrene and related monomers.

In Table 5.3 are a number of insoluble powders that have been evaluated in bead polymerization. Some of these solids, such as metal oxides and hydroxides, can be removed after polymerization by their solubility in dilute acids. Since good dispersing action seems to require covering the surface of the monomer droplets, the amount of dispersing powder depends upon the de-

TABLE 5.3
Some Insoluble Suspending Agents

Powdered kaolin, BaSO$_4$, talcum, Al(OH)$_3$	O. Roehm, E. Trommsdorff, Ger. 735,284 and 747,596 (Roehm)
Hydrolyzed Mg silicate	H. T. Neher et. al., U.S. 2,440,808 (R & H)
Bentonite + gelatin + inorg. salts	R. N. Haward, U.S. 2,665,270 (Petrocarbon)
Silicic acid + emulsifier	Brit. 952,351 (Dow)
Titanium dioxide	R. N. Haward et. al., Brit. 710,498 (Petrocarbon)
Mg(OH)$_2$ + little oxalic acid	A. Tanaka et. al., Japan 67-19,242 (Daicell)
Fe or Al hydroxide + polymethacrylic acid + emulsifier	G. Richter, Ger. (East) 43,896
Basic zinc carbonate + alkyl ammonium propionate	C. P. Ronden, U.S. 3,462,380 (Dow)
CaCO$_3$ + fatty acid	F. Wolf, Ger. (East) 68,631
MgCO$_3$ + PVA	E. F. Jordan, U.S. 2,810,715 (USA)
Zinc oxide	A. K. John, U.S. 3,442,881 (Dow)
Calcium phosphate + emulsifier	J. M. Grim, U.S. 2,673,194 (Koppers)
Calcium oxalate + emulsifier	E. Zancker, Ger. (East) 15,244 (Buna)

sired size of the droplets. As a rule from 0.1 to 1.0% in water is practical. In order to obtain powders of very small size their preparation by precipitation may be carried out in aqueous phase directly before use in suspension polymerization (6,48). Only very small concentrations of surfactant as added by Grim promote dispersion of the phosphate powders and give successful bead polymerizations. Such surfactants control the wetting angle and thereby the dispersing action, apparently also by adsorption on the particle surfaces. The adsorption may be purely physical or by chemisorption. Any excess of true surfactant may cause serious losses of polymer as latex fines. The emulsion studies of Wenning (11) help to clarify these phenomena.

IV. PREPARATION OF MULTIPHASE PLASTICS

The use of bead polymerization systems is not restricted to manufacture of ordinary homo- and copolymers. A recent outstanding application is the preparation of high-impact plastics and other complex, multiphase copolymers. These processes, which involve more or less graft copolymerization of monomers to rubberlike components, often involve several steps and transitions between different types of systems. The very large patent literature on preparation of high-impact plastics can not be surveyed here, but only some applications of bead polymerization.

A simple, but not very useful, method proposed for graft copolymerization

is to contact polymer beads with another miscible monomer in aqueous suspension and then complete polymerization (49). Practical methods for graft copolymerization include reaction of monomers with preformed elastomers containing double bonds (such as butadiene polymers), transesterification of vinyl copolymers by methacrylic acid and by chain transfer e.g., through alpha hydrogen atoms of acrylate polymers.

A three-step suspension polyfterization for preparing high-impact methacrylate polymers was suggested by successive polymerization of MMA, butyl acrylate and again MMA (50). However, in practice the preformed elastomer such as butadiene, acrylate ester, or ethylene–vinyl ester polymer generally is first dissolved or dispersed in the larger proportion of monomers which will form the hard or resinous phase (styrene, acrylonitrile, MMA, or their mixtures). Then this viscous solution is introduced into a reactor for bead polymerization. The addition of a little solvent has been suggested in order to improve miscibility and to give more homogeneous products (51). The solvent may be allowed to escape during polymerization. There is danger in the use of elastomers prepared by emulsion polymerization containing variable amounts of residual surface active agents that can impair yields of bead copolymers. However, under certain conditions direct transition from emulsion to suspension polymerization has been described. Thus plastics with a high content of viscous elastomer phase have been prepared experimentally without first isolating the pure elastomer. Graft copolymers of MMA with crosslinked polybutylacrylate were copolymerized in suspension with MMA using polymethacrylic acid as suspending agent to give bead polymers (52). Latex has been mixed with monomer and then partially coagulated by acidification and then submitted to suspension copolymerization with larger proportions of monomer (53). Not all such suggestions in patents prove practical.

The properties of high-impact two-phase plastics depend very much upon the degree of dispersion of the elastomer phase. In many cases elastomer particles of 1–10 microns are best. For best control of particle size the elastomer dispersion with the resin-forming monomer is first partially polymerized in bulk and then finished in bead-type aqueous suspension. For example, a polybutadiene or partially crosslinked polybutadiene copolymer dispersed in styrene may be copolymerized in bulk until inversion of phases occurs so that elastomer particles are then dispersed in the continuous styrene–polystyrene phase. Polymerization then can be completed either in bulk with special methods for heat removal and agitation, or by suspension polymerization. The degree of dispersion of the toughening phase is determined by a number of factors such as the fraction grafted and the character of agitation used (54). Addition of a second elastomer after phase inversion also has been suggested (55).

V. SUSPENSION POLYMERIZATIONS FROM NONAQUEOUS MEDIA

In recent years processes have been developed in which organic liquids form the outer, dispersing phase. It is important to distinguish the polymerization reactions having their locus within the hydrophilic phase from those occurring in hydrophobic phase. Both types have commercial utility.

Stirred polymerizations of homogeneous solutions of monomers such as vinyl chloride and acrylonitrile have some resemblance to suspension polymerizations after insoluble polymer begins to form. Powders, granules, or polymer masses may form, but seldom spherical, clear beads. These have been called precipitation polymerizations. However, a commercial process uses polyvinyl pyrrolidone as a suspension stabilizer in methanol to form beads of styrene–acrylonitrile copolymer (56). A study of such processes confirmed that most of the polymerization occurs in the solution phase rather than in the precipitated phase (57). The separation of the solid copolymer occurs earlier from higher proportions of methanol and at lower temperatures.

The formation of such a second phase of polymer may result in copolymerizations involving crosslinking (58). For example, from a hydrophilic organic solvent such as ethoxyethanol mixtures of acrylic acid, acrylic esters and polyfunctional crosslinking monomers were reported to form bead products. Soluble dispersing polymers or protective colloids were added. Initial two-phase copolymerization of acrylamide with quaternary ammonium methacrylic derivatives in water–acetone or water–alcohol mixtures gave granular water-soluble products (59).

So-called reverse suspension or "reverse emulsion" polymerizations, which recently have attained commercial importance, begin with concentrated aqueous solutions of monomers dispersed in hydrophobic organic solvents (60). The technique is particularly useful with acrylamide, methacrylamide, salts of the corresponding acids, and quaternary ammonium monomers such as quaternized diethylaminoethyl methacrylate and vinylbenzyl trimethyl-ammonium chloride and their mixtures. Generally 50–80% monomer in concentrated solution with water is dispersed along with water-soluble initiators such as persulfates, hydrogen peroxide, and redox activators of these. As external phases one may use aliphatic hydrocarbons or less frequently toluene, xylene or chlorinated hydrocarbons. In one example of Nalco the following dispersion free of air was reacted with persulfate initiator giving a peak temperature of 55°C:

Acrylamide	53.4 p	Isoparaffin hydrocarbon	72.0
Acrylic Acid	22.8	Toluene	1.7
NaOH	12.7	Sorbitan monostearate	3.8
Water	101.0		

The beads generally have nearly spherical form, which simplifies their characterizations. However, under certain conditions the shapes deviate from spherical, which may have advantages in special applications.

Bead size usually is measured by conventional shaking sieves for sizes of 0.1 mm and above. For very fine beads a sucking or wet sieve often is needed because of the strong electrostatic charge resulting from the high surface to volume ratio. The sieving process may be improved also by addition of water, surfactants, pigments, or electrical conductors in order to reduce static charge. Less common methods for determining particle size include microscopic observations, analytic air sifting, sedimentation, and use of a Coulter Counter. For evaluation of sieve analyses the plot of sieve width against the percentage residue is useful. The average particle size is given by the 50% value, or the size of a hypothetical sieve that would pass 50% of the beads. Similarly the breadth of distribution may be characterized by the ratio of sieve size for 30% to that for 70% residue (36). The evaluation of particle size is facilitated when the plot of per cent residue against sieve size gives a logarithmic plot. Examination of a series of commercial bead MMA polymers and styrene polymers showed that this condition is possible in the case of small and medium-sized beads. As a measure of size distribution the standard deviation may be used, which in most cases ranges from 20 to 30%.

Of interest in judging the reproducibility of bead polymerizations is the average bead size. Control tests on bead polymers of Röhm at Darmstadt showed that the average bead sizes from a large number of production lots followed a normal Gaussian distribution. The standard deviations depending upon the particular monomers and reactors studied.

We have discussed effects upon bead size of hydrodynamic conditions rates of stirring, type and amounts of added dispersing agents. Contraction during polymerization also reduces bead size appreciably. Although effects of such parameters have been much investigated the results usually apply only for the particular monomers and reactors studied. In 1964 Hopff and co-workers began publication of systematic studies of bead size (36,41,47). Bead size from suspension polymerization in geometrically similar reactors was related to the following parameters:

D, d Diameters of kettle and stirrer, cm
n Rotations of the stirrer, per sec
η_w, η_m Viscosities of water and monomer, g/cm-sec
δ_w, δ_m Density of aqueous and monomer phases, g/cm^3
σ Surface tension g/sec^2

In research with MMA Hopff and co-workers chose relatively high concentrations of partially saponified polyvinyl acetate as dispersing agent in order

Effective suspension stabilizers include fine powders such as hydrophobic kaolin and bentonite, silanized silicic acid, or mineral fillers together with emulsifiers that are dispersible in organic medium. Other suspension stabilizers include sorbitol oleate and soluble polymers bearing hydrophilic substituents such as COOH, SO_3H, and NH_2 groups, especially compounds with a favorable hydrophilic to higher hydrophobic ratio of groups. In such reverse suspension polymerizations graft and block copolymers may be particularly effective agents when one polymer component is solvated by the monomer phase and the other by the continuous organic medium (60). Related systems have been called reverse emulsion polymerizations which give viscous latices (61). These latices, however, have different properties from conventional aqueous latices.

These reverse processes may be carried out by addition of the monomer-containing phase to the immiscible organic phase with stirring. The heat of polymerization may be removed by reflux of the volatile organic liquid. In order to keep the polymerization temperature low, and the polymer free from crosslinked fractions it was suggested that acrylamide be polymerized with redox initiation at reflux under reduced pressure (62). Acrylamide-acrylic acid polymers of very high molecular weight are manufactured from water in paraffin dispersion for use as flocculating agents. The granules may be washed with dry acetone. In the suspension polymerization of acrylic acid in presence of boiling heptane small amounts of inhibitor were added to prevent precipitation polymerization in the organic phase (63). In a patent example, acrylamide polymer particles were separated from suspension in xylene by centrifuging (64). Fine dispersions of MMA copolymers in alkanes for use in coatings have been developed by ICI, PPG, and others (65).

In the copolymerization of maleic anhydride with vinyl ethers or with vinyl esters in organic solvents by heating in presence of azo or peroxide initiators, the system is homogeneous initially before the copolymers form a solid separate phase. For obtaining granular products from these copolymerizations the additions of copolymers of styrene with higher alkyl acrylates was disclosed as dispersing agents, as well as copolymers with vinylpyridine, dimethylaminoalkyl methacrylate, or N-vinyl pyrrolidone (66).

VI. BEAD SIZE

Control and measurement of bead size is important for specific applications. Thus for dental prostheses by the monomer-polymer or Mo-Po process (where slurries of swollen polymer beads in monomer are shaped for final polymerization) fine beads below 0.1 mm diameter are needed. Beads for use in plastic extrusion and molding may range from 0.2 to 0.5 mm. For polystyrene foam and ion exchange resins beads of 1 mm and larger are supplied.

to avoid nonlinear influences of the amount of dispersing agent upon surface tension. They found under these conditions that the ratio of the two phases and gravitational acceleration did not affect bead size. Based upon dimensional analysis and experimental determination of exponents they proposed the following equation for bead size L_0:

$$L_0 = \frac{A \cdot \sigma_0^{0.1} \cdot \eta_m^{0.1} \cdot \sigma_w^{0.5}}{D \cdot n^{1.5} \cdot \eta_w^{0.6} \cdot \delta_m^{0.5}}$$

A is a constant, while d is not needed because of its proportionalitl to D. Dispersing agent and monomers are not included implicitly. Initiators and polymerization auxiliaries apparently do not influence bead size as long as they do not affect η_m, δ_m, and σ_0. Since these three values change during the course of polymerization, they must be determined actually as complex functions of time, temperature, and rate of polymerization. However, such complex analysis was found unnecessary because the monomer in a few minutes after starting agitation was dispersed as stable drops from which practically no change occurred thereafter. The surface tension of the solutions fell with increasing concentration of suspending agent to a limiting value depending upon the type of agent. Only in this limiting range of surface tension was there a proportionality between surface tension and bead size in experiments with partially saponified polyvinyl acetate, methyl cellulose, carboxymethyl cellulose, and polyethylene oxide. On reducing the amount of suspending agent, also on increasing the surface tension, the bead size remained almost unchanged, but did increase sharply at very low concentrations of suspending agents. These observations of Hopf and co-workers may not apply to most commercial suspension polymerizations, which use only small concentrations of suspending agents and where the effect of surface tension on bead size plays a less important role.

Bead size is also influenced by the geometry of the reaction vessel, the type of stirrer, and its rate of rotation. For example, impeller agitators together with a breaker plate produce finer beads than leaf or anchor agitators. The exponent of the stirring speed depends upon the type of stirrer and also can be influenced by small concentrations of suspending agents. While the densities of the monomer and water phase can not be controlled freely in practice for determining bead size, higher viscosities from dissolved polymer in the monomer phase can sharply increase bead size. This is applied widely in those commercial processes in which certain conversion is first reached before the largest proportion of the suspending agent is added (68).

There are some special processes for preparation of particular bead sizes. For example large polystyrene beads with narrow distribution of size have been made by continuous addition of styrene to preformed beads in aqueous dispersion at the same rate at which monomer is consumed (69).

VII. PROCEDURES FOR SUSPENSION POLYMERIZATION

A. Apparatus

For operation at normal pressure in the laboratory three- or four-necked glass reactors with suitable stirrer, reflux condenser and inlet tube are generally chosen (Fig. 5.5). Heating and cooling may be provided with a water bath. The use of shaking autoclaves or shaking flasks and agitation by magnetic means are less satisfactory than uniform stirring. However, the former may be used for polymerizations under pressure if no suitable stirred pressure vessel or autoclave is available. Molecular oxygen is usually excluded unless this is found unnecessary.

Hopf and co-workers investigated the dependence of bead size upon the "apparatus constants" of polymerization vessels (36, 67). For this purpose they used cylindrical stirred vessels of different volume of the same diameter and filled depth equipped with square blade agitators mounted in the middle of the liquid. They found that the intensity of mixing as related to the diameter of the stirrer and its rate of rotation largely determined the droplet size before any polymerization reaction had occurred, and this in large part determined the final bead size. However, other parameters in most industrial
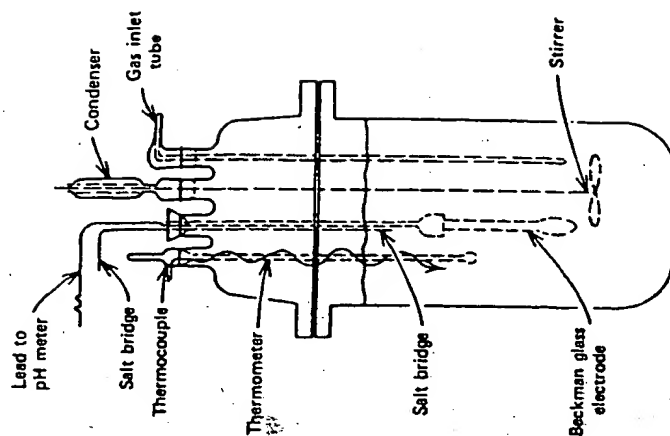

Fig. 5.5. Schematic drawing of glass reactor suitable for experimental suspension polymerization. Kaghan and Shreve, Ind. Eng. Chem., 45:294 (1953).

processes also affect bead size, such as surface tension, viscosities, and amount of suspending agent.

Commercial equipment for production of bead polymers may consist of a system of connecting units. See Fig. 12 in ref. (1). Large polymerization kettles or autoclaves have up to 30 cu meters' capacity. Heating and cooling are controlled by fluid flow through a jacket or mantle, or sometimes through internal pipes. The inner surfaces of such reactors are of smooth-finished enamel or stainless steel. Because of HCl evolution in polymerization of vinyl chloride enamel vessels must be used. The different agitation systems and forms of stirrers employed range from turbines and impeller stirrers to the frequent blade and anchor agitators, with or without breaker plates. It is essential that besides horizontal motion the liquid particles receive enough vertical mixing. This may avoid creaming of the monomer droplets at the beginning and settling of the resulting polymer beads near the end of the reaction. Since the intensity of stirring at the beginning of the process is critical for bead size an agitator of variable rate of rotation is needed. In some cases a combination of very fast and slow acting agitators was recommended (70, 71). Kettle and agitator designs should be coordinated so that there are no dead unagitated corners in which coalescence or precipitation of polymer can occur.

Charging of the reaction vessel with water, suspending agent, monomer and polymerization agents occurs through pipes by gravity or pumps from storage tanks, or from vessels in which the reactant solutions have been prepared. Often several polymerization reactors are connected with one large stirred vessel which holds several polymer charges in mixture or for after-treatment such as dissolving in acid powder-type suspending agents. Washing and separation of the beads usually are accomplished by use of continuously operating centrifuges (shell type), sieves, or filters. For small charges the beads may be separated on a Nutsch filter. According to the particle size and treatment the solid beads then may contain 5-40 % water. The beads may be dried using a continuous plate drier, flowing bed drier, or similar equipment. The drying must be at temperatures below the glass temperature (t_g) of the polymer.

B. Technical Procedures

Methods and equipment in suspension polymerization vary with properties of the starting materials and of the end products. A gaseous monomer such as vinyl chloride is polymerized in pressure reactors. Styrene, acrylic, and methacrylic esters, as well as vinyl acetate can be polymerized at atmospheric pressure. However, for these one operates usually just above 760 mm without reflux under autogenous pressure.

The monomers may be added in purified form free of inhibitor to demin-

eralized water. Oxygen is excluded from the polymerization apparatus by layering or by evacuation and saturating with inert gas. For better utilization of the equipment and economy of time, one often starts with preheated water. The usual range of commercial ratios of monomer to water (1:1 to 1:3 by weight) may be lower still in the case of very rapidly polymerizing monomers such as tetrafluoroethylene. The heat of polymerization is controlled by external cooling, but in emergencies cold water may be injected into the kettle.

Some commercial suspension polymerizations are still carried out under reflux condensers in which the returning condensed and cooled monomer-water mixture provides heat exchange. Reflux with intensive mixing with rapid turbine stirrer was recommended (70). Exotherm peaks such as result from the gel effect can thus be dissipated. The occurrence of temperature peaks can be reduced in these processes by adding initiator gradually at a rate similar to that at which it is used. In some cases there are advantages in polymerizing at the boiling point of the monomer-water mixture and regulating the monomer addition rate so that the reflux rate remains constant.

The temperature cycle in suspension polymerization affects molecular weight distribution and may affect branching, grafting, and tacticity. For example, MMA prepared at lower temperatures tends to be somewhat more syndiotactic. In general the temperature is kept as constant as possible during polymerization. Starting with water preheated to the polymerization temperature has the additional advantage of preventing the formation of a fraction of polymer of very high molecular weight during the heating-up period. It has been suggested that the temperature be raised when the gel effect begins in styrene-acrylonitrile copolymerization in order to overcome excessive increase in molecular weight (72). In actual practice it is more often necessary to cool the reactor at the onset of the gel effect in order to prevent dangerous runaway reaction. In large commercial systems the temperature program may be guided continuously by electronic means from the internal reactor temperature. It has been suggested to inject a volatile substance of low solubility such as a hydrocarbon into the reaction space from which the reaction rate may be regulated by observing the pressure (73).

The temperature difference between the kettle wall and the reaction mixture should be small in order to prevent polymer deposits on the walls (74). After polymerization is finished the emptied reactor is cleaned by spraying with water. Usually after several charges it is unavoidable to remove adhering polymer deposits or growths of polymer, which must be done very carefully in the case of enameled or glass-lined vessels. In such reactors cleaning by organic solvents may be needed. This can require 1-2 days for polystyrene, 12-24 hours for polyvinyl chloride and 4-6 hours for MMA polymers. Recently polyurethane, silica and other smooth coatings are said to reduce polymer deposits on reactor walls.

The time required for polymerization can be often reduced by employing

combinations of several initiators of different half life or temperature of activity. Acceleration by using higher temperatures is impractical in many cases, however. For example, vinyl chloride must be polymerized below 60°C because of excessive formation of HCl and chain branching, as well as degradation of the polymer invariably resulting from higher temperatures.

C. Continuous Processes

Although seldom employed on a commercial scale, continuous bead processes have been studied in the laboratory and on a pilot plant scale. Polymerization was suggested in a vertical tubular reactor that was widened to a conical shape at the top (75). Inside was mounted a long, vertical rotating agitator with stirring arms at different distances. The cylinder was filled with aqueous phase and monomer of lower density dispersed as droplets in the top portion. Continuously as polymerization occurred the monomer–polymer phase became higher in a density than the outer phase and fell into the lower zone and finally was withdrawn at the bottom. A similar process using viscous monomer–polymer solution was proposed (76). A series of successive reaction vessels has been suggested similar to those empolyed for continuous emulsion polymerization (77). One of the greatest difficulties encountered in continuous successive zone reactors is obstruction by polymer agglomerates and deposits on the walls, which has a great tendency to occur in suspension polymerization. In continuous copolymerization of styrene and acrylonitrile (75:25) bentonite was added to the aqueous phase in order to prevent agglomeration (78). Many other continuous suspension processes have been tried on a small scale.

D. Aftertreatment of Bead Polymers

Treatments of bead polymers resulting from suspension polymerization must take into consideration their large surface, which on one hand facilitates loss of volatile impurities, but also promotes adsorption and holding of impurities such as dust by static charge. The first purification step may consist in removal of unreacted monomer and water at elevated temperatures but without producing undesirable side reactions such as polymer degradation and grafting reactions. In the case of vinyl chloride suspension polymerization, as much as 40% of the initial toxic monomer must be recovered with safety precautions under reduced pressure or by blowing out with inert gas. Small proportions of residual styrene may be distilled out at slightly elevated pressure at 145°C (79). Removal of residual monomer by extraction with alcohol has been proposed (80).

The separation of residual monomer may be very important from polymers that undergo undesirable chemical change before the end of polymerization.

Thus in copolymerizations residual monomer near the end of reaction may form polymer of unfavorable qualities. An example is the preparation of high acrylonitrile copolymers in which the last fraction formed may tend to be discolored (81).

Complete separation of residual monomers and impurities of low vapor pressure generally is not possible by conventional drying processes. Such residues are held fast by their solubility and inclusion in the polymer product. High temperatures are often excluded by thermoplastic granules adhering to one another, also by polymer degradation or cracking to free monomer. However, treatment of polymer compositions for use as molding plastics, as carried out in extruders with evacuation zones of low pressure, often succeeds in removing residual monomer, water, and other volatile impurities.

Unless the bead polymers are used in pigmented form, the insoluble type of suspending agent such as calcium phosphates must be removed. Simple washing may be satisfactory. However, treatment with dilute mineral acid is necessary to remove dispersing agents such as magnesium carbonate and aluminum hydroxide. Optimum pH values have been found for removal of insoluble suspending agents as well as residual suspending agents based on methacrylic acid copolymers by washing in the presence of nonionic detergent (82). Because of difficulties in complete removal of haze-forming impurities from suspension polymers, there is a trend toward improved methods of bulk polymerization for manufacture of molding plastics of high clarity.

The trickling or flow properties of moist and dried beads affect filtering and subsequent application technologies. These properties especially may be influenced by residues of organic polymeric dispersing agents on the surfaces. Centrifuging, washing, and filtering may separate any fraction of polymer that occurred by an emulsion process. By the choice of suspending agents the coagulation of this small latex fraction can be prevented from clogging and stopping filtration. Small additions of surfactants in the last wash water have been reported to reduce the amount of residual water which must be removed by drying in an oven (83). Partial reuse of aqueous phase for a succeeding suspension polymerization has been suggested (84).

Both continuous and discontinuous methods are used for drying polymer beads by ovens, multiple layer, or flight driers. Vacuum driers may be used for polymers of low softening temperature. For absolute polymer clarity, great care must be taken in drying to prevent contamination by dust from the air. The drying at elevated temperature also may eliminate catalyst residues and odors.

E. Incorporation of Auxiliary Agents

Addition of stabilizers or other auxiliaries to beads as formed suspended in

the aqueous phase may have special advantages. For example, regulator-free MMA polymer beads were heated in a closed kettle with added aliphatic mercaptan and agitation for 10–30 min at 125°C. In this way the polymer was stabilized to withstand later heat in molding (85). For preparing expandable or foamable beads of styrene polymer, volatile hydrocarbons may be incorporated at elevated temperatures and pressures into bead polymers (86). Direct coloring of dispersed beads by organic dyes has been suggested (87). Rosin and abietic acid may be added to polyvinyl acetate beads to prevent adhesion on storage (88). Other solid additives such as pigments and solid blowing agents, such as azo compounds, are better added to the dried beads and then further incorporated in extruders or mixers (89). The agents become bound to the thermoplastics by the heat generated.

F. Electrostatic Charge and Trickle

The trickle or flow behavior of the dried beads is important in their transfer from vessels by gravity or pneumatic means, also for sieving and mixing processes. Generally hard plastic beads flow well enough except when bearing excessive electric charge. Many plastics have high surface resistance and low electrical conductivity. Mechanical action in moving and mixing the beads can promote high electrostatic surface charges. Rubbing of beads on container walls can lead to either positive or negative charges (90). The influence of excess electrostatic charge upon the trickle behavior especially causes difficulty in fine bead polymers that are very dry. Removal of the charge or exchange of charge between particles are desirable (91). Use of ionizing plasmas is not feasible. A different process using the action of ionized air on the charged beads has been proposed (91). Rate of neutralization of the charged surfaces can be accelerated by adding small amounts of water. The formation of water films on the bead surfaces can be promoted by small additions of polyethylene glycol, surfactants (92), or by chemical treatment of the beads, such as sulfonation (93). However, such processes all change the properties of the plastics more or less adversely. A different process using the action of ionized air on the charged beads has been proposed (91).

G. Soft Beads

The processes described so far for separation from aqueous phase and aftertreatments apply to relatively hard beads having glass temperatures sufficiently high for drying and storing in bead form. Beads formed from polymers of long chain alkyl acrylates and methacrylates tend to adhere to each other before they can be separated from aqueous phase and dried. However, some of these monomers form relatively stable, fine bead suspensions and emulsion polymers, which are useful directly, for example, as binding agents for fibers (94).

H. Difficulties in Bead Polymerization

The actions of stabilizing agents in suspension polymerizations have been studied and reviewed continually in order to prevent failures by agglomeration of the dispersed phase, which can form one large unmanageable mass. Such disasters are much feared since the heat of polymerization can no longer be removed from the large reacting mass, obstruction of the kettle openings can result, and dangerous inner pressures can develop. The hardened polymerization mass may be extremely difficult to remove from the kettle interior, eg, by compressed air drill. Methods for prompt detection of failures in suspension polymerizations were discussed (95).

Sticking together of some loose beads or union of some of the droplets may leave a fraction of suspending agent within the beads and thus impair the clarity of the plastics therefrom. Thus in polystyrene beads made using ^{14}C-labeled hydroxyapatite as suspending agent, higher radioactivity was found in the fraction of larger granules (96). Objectionable turbidity may result also from incomplete removal of electrolytes from the water, which on drying remain on the bead surface. Grafting reactions also may produce poor trickle of beads; for example, some polyvinyl alcohol may be fixed to the surface in this way. Such coatings also may impair the solubility of the beads. Fractions of extremely small particles resulting from side emulsion polymerization may be minimized by adding small amounts of water-soluble inhibitors such as thiourea or copper salts (97). Such fractions reduce yields and may pollute the waste water or air. Coagulated fractions as dried crusts can impair uniformity because of their usual much higher molecular weight. The worst effects which these cause are so-called fish eyes and streaks in extruded sheets and films.

Growths of polymer upon reactor walls also may be a problem. Because of their different molecular weight such accretions should not become mixed with the polymer products. These occlusions of polymer also may impair heat exchange and prevent continued use of the kettle. Deposits are smaller if there is only a small temperature gradient at the walls during polymerization. Use of reflux for temperature control may compensate for poor heat exchange through the jacket (70). However, the liquid returned from reflux may cause sticking together of beads.

VIII. COMMERCIAL PRODUCTS WITH EXAMPLES OF PREPARATION

A. Methacrylate Ester Polymer Plastics

Methyl methacrylate-based polymers of different molecular weight ranges and softening behaviors are used for injection molding and extrusion. Poly-

mers of average molecular weight 100,000–200,000 are usually prepared in presence of long alkyl mercaptans or esters of thioglycolic acid. The softening range and melt viscosity may be controlled also by copolymerization with minor proportions of alkyl acrylates or other comonomers. Usually molding lubricants, antioxidant or other stabilizers, UV-absorbing agents, etc., also are added. The bead sizes of these range from 0.2 to 0.5 mm. A plastic copolymer with resistance to stress crazing was prepared from the following (98):

Water phase:	
Deionized water	100 parts
Sodium polymethacrylate	0.03
Na$_2$HPO$_4$ (buffer)	0.3

Monomer phase:	
MMA	92
n-Butyl acrylate	8
Stearyl alcohol	1
Lauroyl peroxide	0.5
t-Dodecyl mercaptan	0.4

In a kettle reactor the monomer phase was dispersed in the aqueous phase under strong agitation. Oxygen dissolved in the system was largely removed by evacuation and flushing with pure nitrogen. The mixture then was heated to 80°C and maintained at that temperature until the heat evolved by polymerization was sufficient to produce a temperature rise. The temperature then rose to 95°C. After 10 min the batch was cooled, the beads separated from the water phase, and dried. The beads may be used for molding as such or first extruded to form larger granules for better fabrication properties. The plastic had a Vicat softening temperature of 99.1°C, a melt viscosity of 2.4 kp at 240°C, and a specific viscosity of 0.71 (1% in chloroform). Recently MMA has been copolymerized with thioalkyl methacrylates (for improved chemical stability in tests at 260°C for 1 hr) (99).

B. Lacquer MMA Copolymers

For preparing solutions in organic solvents for use in lacquers and adhesives copolymers of lower specific viscosity and good solubility can be prepared such as the following (100):

Water phase:	
Deionized water	300 p
MgCO$_3$	1.0
Sodium alkyl sulfonate	0.01

Monomer phase:	
Isobutyl methacrylate	87
2-Ethylhexyl acrylate	10
2-Hydroxypropyl acrylate	3
Lauroyl peroxide	0.5

In a kettle equipped with agitator, thermometer, and reflux condenser, the MgCO$_3$ is dispersed with addition of the alkyl sulfonate and CO$_2$, and the aqueous phase heated to 75°C. At this temperature the monomer phase is introduced and the temperature maintained at 75–77°C. About 90 min after the monomer has dispersed, the inner temperature rises about 4°C. After reaching this maximum temperature heating is continued near 75°C for 1 hr; then the contents are cooled and the MgCO$_3$ dissolved at 40°C by adding 10% hydrochloric acid solution. The beads are separated on a Nutsch filter, washed until acid free by deionized water, and then dried. Azo initiators may be used instead of peroxides in suspension copolymerizations of methacrylate esters.

C. Crosslinked Macroporous Beads

These have achieved industrial importance for chromatography and adsorption, and their derivatives are used as ion exchange resins. The macroporous structure, which combines large inner surface with adequate strength, is obtained by polymerization in presence of a liquid miscible with the monomer but only capable of swelling the polymer. As an example, a solution of 41.1 g MgSO$_4$·7H$_2$O dissolved in 110 g water was placed in a cylindrical reactor with agitator (101). There was added with stirring a solution of 11.31 g NaOH in 34.25 g water. In this aqueous phase containing 1.5% suspended Mg(OH)$_2$, was dispersed the following monomer phase:

48.42 ml ethylene glycol monomethacrylate	
4.98 ml ethylene glycol dimethacrylate	
0.25 g lauroyl peroxide	
25 ml toluene	

After 10 min stirring at 25°C the temperature was raised to 60°C. During 2 hr of reaction beads of swollen copolymer were formed. The reaction was completed by addition of a near equivalent amount of HCl, the beads were dissolved by an additional hr at the same temperature. The Mg(OH)$_2$ was filtered off, washed, and dried.

D. Polystyrene Plastics

Styrene is often polymerized in aqueous suspension to give beads of diameter between 0.25 and 1.0 mm especially for dry coloring. Because of the slow rate of styrene polymerization and the necessity to reach fairly high molecular weight, the polymerization is generally not carried out isothermally but with stepwise rise of temperature. For this purpose one needs to use a mixture of several initiators having different temperatures of decomposition to free radicals. The half life of one initiator should be similar to the polymerization time in the temperature range. As example of preparation [...]

Aqueous phase: 16.6 kg demineralized water
0.242 kg $Ca_3(PO_4)_2$ paste (50%); preparation (103)
0.143 kg Na-β-naphthalene sulfonate
0.077 kg 15% aqueous Na polyacrylate solution

Monomer phase: 16.6 kg styrene
0.012 kg azobisisobutyronitrile
0.006 kg benzoyl peroxide
0.015 kg t-butyl perbenzoate

In a glass autoclave of 38 liters the styrene and calcium phosphate are dispersed with agitation in water at 30°C. Finally the initiators are mixed in after warming at 40°C. Then the air is replaced by nitrogen, the reaction vessel is closed, and the following temperature program followed:

Hours	Temperature, °C	Hours	Temperature, °C
0–1	40–80	8–13	90
1–7	80	13–15	90–110
7–8	80–90	15–27	110

Finally the dispersed product is cooled to room temperature brought to pH 1 by HCl to dissolve the suspending agent, the beads separated, washed with water, and dried.

Most "polystyrene plastics" are now copolymers, for example styrene-methacrylic acid where 5 parts of the latter were added during 2 hr copolymerization at 90°C (104).

E. Expandable Polystyrene Beads

For preparation of foamed material for insulation and packaging purposes, expandable polystyrene beads of 0.2–2.5 mm diameter containing occluded droplets of blowing agent are made (Fig. 5.3). On heating at 85–95°C the beads expand about 20 times. The foamed form may be completed by use of superheated steam.

An example follows (105). One dissolves 10 parts of emulsion polymerized polystyrene of Fikentscher K-value 90 which is free of emulsifier residues in 90 parts styrene and adds 0.45 part benzoyl peroxide and 7.5 parts pentane. This solution is added to a stirred kettle containing a solution of 0.8 part sodium pyrophosphate and 0.8 part of a copolymer from 90 parts vinyl pyrrolidone and 10 parts methyl acrylate (K-value 90) dissolved in 300 parts water. The polymerization required 20 hr at 70°C and 15 hr at 90°C. When 60% conversion was reached 15 hr after starting, nitrogen pressure was applied to maintain 4.5 atm. There was obtained lump-free, spherical beads especially suitable for expansion to packaging foam.

F. Polyvinyl Chlorides

Many special types of vinyl chloride polymer powders are supplied to satisfy diverse methods of fabrication and uses. Suspension polymers for unplasticized applications as well as with plasticizer, e.g., for electrical wire and cable insulation as well as for molding. The white powder supplied for hard moldings contains (besides compact, glassy grains) some particles with rougher surfaces for absorbing stabilizers and lubricants. For plasticizer reception the PVC grains preferably have rough segmented surfaces (Fig. 5.6). These particles give desirable crumbly, nonsmeary mixtures with plasticizer that behave well in fabrication equipment. For plasticizer-free plastics, copolymers of vinyl chloride with 20% maleate ester or 10–15% vinyl acetate also are used. An example of synthesis of easily plasticized PVC follows (106):

Water	180
Polyvinyl alcohol	0.5
Sodium isobutylnaphthalene sulfonate	0.03
Vinyl chloride	100
Lauroyl peroxide	0.5
n-Butane	3.0

The vinyl chloride dispersed in the water phase under pressure is warmed 8 hr at 52°C. The butane promotes formation of porous polymer particles quickly swollen by plasticizers. There is formed about 75 parts of polymer of K-value 70 and average grain size between 50 and 150 microns. It is quickly plasticized by 30% of dioctyl phthalate at 130°C. Without use of butane about three times as long is required for swelling with plasticizer. For hard

Fig. 5.6. Particles of suspension PVC with rough surfaces, enlarged 37 x and 720 x. BASF, Ludwigshafen.

POLYMERIZATIONS IN SUSPENSION

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Examples of control of PVC molecular weight by reaction temperature are shown below:

Deionized water	6000 kg		
Polyvinyl alcohol	5		
Vinyl chloride	3000		
Benzoyl peroxide	4.0		

	40°C	50°C	60°C
Polymerization temperature			
Viscosity number, ml / gm	143–170	116–132	88–106
K-value (Fikentscher)	75–80	68–72	60–65

The polyvinyl alcohol dispersing agent above is 80–85% saponified polyvinyl acetate of high viscosity and saponification number 100–130. It is added as a 5% solution in water. In order to avoid formation of fractions of low molecular weight the polymerization carried out at 40°C was stopped after 50 hr at 65% conversion. The reaction time at 40°C can be shortened by using isopropyl percarbonate as initiator.

In order to obtain porous beads or pearls 10 to 20% of the kettle contents may be withdrawn after 45–50% conversion. The sudden fall in pressure produces porous particles. The remainder is reacted further to 90–95% conversion. The pressure in the reactor remains fairly constant (e.g., 115 psi at 55°C) until about 70% conversion, when it declines quickly. Droplets persist until about 75% conversion when all of the monomer is absorbed by the solid polymer particles. During the 16 hr of polymerization the organic phase contracts about 35%.

In current industrial suspension polymerizations highly reactive percarbonate initiators are often used, for example, isopropyl percarbonate at 54°C with hydroxypropyl methyl cellulose as suspending agent (107). Unstable diethyl percarbonate was formed in situ before suspension polymerization of vinyl chloride (108). PVC was prepared at 40°C in aqueous suspension initiated by boron alkyls and a small amount of oxygen (109).

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H. Methacrylic Water-Soluble Polymers

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Acknowledgment is made to W. Köhler for literature search and to C. E. Schildknecht for translation of this chapter.

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Benzoyl peroxide	4.0		

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K-value (Fikentscher)	75–80	68–72	60–65

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6. EMULSION POLYMERIZATION

JOHN L. GARDON, M AND T CHEMICALS, INC. *Southfield, Michigan*

I. INTRODUCTION

A large portion of industrial polymers is manufactured in emulsion. Many synthetic rubbers and structural plastics are made from coagulated or spray-dried latexes. Emulsion polymers are the bases of aqueous paints, of adhesives, and of finishes for textiles, paper and leather. This latex technology has become a complex empirical art. Subtle modifications in the composition of the recipes or in the method of synthesis can cause commercially significant changes in the end products obtained from vinyl-type or ethylenic monomers. Table 6.1 shows some types of chemicals that are commonly incorporated into industrial recipes for emulsion polymerization. Copolymers having a wide range of complicated structures may be prepared. The final properties are greatly influenced by the method of monomer addition, the reaction temperature, the choice of initiators, stabilizers, and chain transfer agents.

Emulsion polymerization offers some unique advantages compared to other free radical processes. The reaction rate and molecular weight may be very high, and the viscosity of the product latex is low and independent of molecular weight. Water provides an ideal heat-transfer medium during the reaction. The latex polymers can be dried safely, without causing fire hazard or air pollution. If the glass transition temperature of the polymer is below the drying temperature, latexes can be dried on surfaces into coherent films. A disadvantage of latex polymers is that they usually contain residual water-sensitive minor components, e.g., surfactants and initiator decomposition products. However proper formulation often can minimize the undesirable effects of these impurities.

The literature of emulsion polymerization contains thousands of technical papers and patents. Scientifically oriented reviews have been published (1-7). Much industrial technology has been summarized by Warson (8). Pamphlets from raw material suppliers (9) provide aid for industrial emulsion polymerizations.

II. BACKGROUND RELEVANT TO THE KINETIC THEORY

A. Experimental Conditions Amenable to Theoretical Analysis

A typical experiment is performed under nitrogen in a three-neck flask

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                //(C08L  33/12
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                    C08L  25:08  .)
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(21)Application number : 59-199451   (71)Applicant : ASAHI CHEM IND CO LTD

(22)Date of filing :   26.09.1984   (72)Inventor :   HAYASHI MASAO

(54) LIGHT-SCATTERING ACRYLIC RESIN COMPOSITION

(57)Abstract:

PURPOSE: To impart high light transmission properties as well as high light scattering properties, by blending a crosslinked polymer and fine inorg. compd. particles with an acrylic resin for use as a material for lighting cover.

CONSTITUTION: 1W20pts.wt. crosslinked polymer and 0.1W5pts.wt. fine inorg. compd. particles are blended with 100pts.wt. acrylic resin. Examples of the acryolic resins are methyl methacrylate homopolymer and copolymers mainly composed of methyl methacrylate. Examples of the crosslinked polymers are polymers having a particle size of 30W300μ obtd. by polymerizing a non- crosslinking monomer mixture of 10W90wt% C1WC4 alkyl methacrylate, 1W50wt% arom. vinyl monomer and 5W50wt% C1WC8 alkyl acrylate and 0.3W3wt% crosslinking monomer. As the fine inorg. compd. powder, at least one member selected from calcium carbonate, barium sulfate, etc. is used, and calcium carbonate is particularly preferred.

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⑫ 公開特許公報（A）　　昭61-78859

㉑Int. Cl.⁴　　　　識別記号　庁内整理番号　　　　㊸公開　昭和61年（1986）4月22日
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　　　33:04)
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　　　25:08)

審査請求　未請求　発明の数 1　（全4頁）

㉒発明の名称　　光散乱性アクリル樹脂組成物

㉑特　願　昭59-195451
㉒出　願　昭59(1984)9月26日

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明　細　書

1. 発明の名称
　光散乱性アクリル樹脂組成物

2. 特許請求の範囲
(1) メタルメタクリレート系重合体100重量部に対して、下記の架橋ポリマーを1～20重量部と無機化合物の微粒子を0.1～3重量部配合して得られる光散乱性アクリル樹脂組成物。ただし架橋ポリマー：
　アルキル基の炭素数1～4のアルキルメタクリレート10～90重量%
　芳香族ビニルモノマー1～80重量%
　アルキル基の炭素数1～8のアルキルアクリレート5～80重量%
とから成る非架橋性モノマーと、架橋性モノマー0.3～3重量%を重合して得られる粒子径30～300μの架橋ポリマー

(2) 無機化合物が、CaCO₃、BaCO₃、BaSO₄、TiO₂、SiO₂、CaF₂、アルミナから選ばれる一種または二種以上から成る特許請求の範囲第(1)項記載の光

散乱性アクリル樹脂組成物。

3. 発明の詳細な説明
（産業上の利用分野）

　本発明はアクリル樹脂中に光散乱剤を分散せしめて、高い光散乱性と高い光透過性とを付与させることにより、照明カバーなどに適した光学特性を有する光散乱性アクリル樹脂組成物に関するものである。

（従来の技術）

　光散乱性アクリル樹脂は、優雅な感覚を与えるさまざまな成形品の成形素材として賞用され、とくに照明カバーや着色用素材として重用されている。

　照明カバー用途に用いるための光散乱性アクリル樹脂に求められる特性は、高い光散乱性を有すると同時に、高い光透過性を兼ね備えていることである。後者の特性は電力エネルギーの効率的使用の面からとくに望まれる特性である。

　光散乱性樹脂を得るためには、アクリル樹脂中に無機物質粉末を含有させることが必要とされ、

―411―

これらの粉末として従来酸化チタン、硫酸バリウム、炭酸バリウム、炭酸カルシウム、二酸化ケイ素などの微粉末が用いられてきた。

（発明が解決しようとする問題点）

しかし、これらの微粉末を添加した樹脂は光散乱性は高いが、光透過性が低いという欠点を有していた。たとえば、照明カバーに使用した場合には、光源が透けて見えない程度に光散乱性を向上させると、光線透過率が低下するため暗く見えるという問題点があった。

（問題点を解決するための手段）

本発明は上記の問題点を解決することを目的としてなされた。本発明者は鋭意研究の結果、光透過性を損うことなく光散乱性を向上させることができる光散乱剤を見出し本発明に達した。

すなわち、本発明における光散乱剤は、メチルメタクリレート／アクリル酸エステル／芳香族ビニルモノマーを主成分とする架橋ポリマーと、従来から使用されている無機物質微粉末とを併用したものであり、これらをアクリル樹脂中に配合分

リレート5～50重量％、芳香族ビニルモノマー1～60重量％とから成る単量体100部あたりに3～3部の架橋性モノマーとを重合することによって得られる粒子径30～300μのポリマーである。

無機物質微粉末としては、炭酸カルシウム、硫酸バリウム、炭酸バリウム、酸化チタン、二酸化ケイ素、フッ化カルシウム、タルクなどから選ばれる一種または二種以上を組み合わせたものであるが、炭酸カルシウムが最も好ましい。

アクリル樹脂100重量部に対して、架橋ポリマーは1～20重量部、無機物質微粉末は0.1～5重量部配合すればよく、好ましくは架橋ポリマーは6～15重量部、無機物質微粉末は0.3～3重量部がよい。

上記架橋ポリマーに用いられるアルキル基が1～8のアルキルアクリレートの代表例としては、エチルアクリレート、ブチルアクリレート、2-エチルヘキシルアクリレート等と、また芳香族ビニルモノマーとしては、スチレン、ビニルトルエ

散することによって目的が達成される。この場合、いずれか一方だけでは目的の効果は発揮されない。

本発明に使用されるアクリル樹脂としては、とくにメタクリル酸メチルを主体とする樹脂があげられ、これにはメチルメタクリレートの単独重合体またはメチルメタクリレートとメチルアクリレート、エチルアクリレート、α-プロピルアクリレート、イソプロピルアクリレート、ブチルアクリレート、アクリロニトリル、スチレンもしくはα-メチルスチレンのいずれか一つ以上との共重合体、またはメチルメタクリレート単独重合体と上記共重合体の混合物が含まれる。上記いずれの場合においても樹脂中に含まれるメチルメタクリレートの割合は50重量％以上であることが好ましい。

本発明の光散乱剤としては、架橋ポリマーと無機物質微粉末との併用物質があげられる。架橋ポリマーとしては、アルキル基の炭素数が1～4のアルキルメタクリレート20～90重量％、アルキル基の炭素数が1～8のアルキルアク

ン、α-メチルスチレン、ハロゲン化スチレン等を、さらに架橋性モノマーとしてはアリルメタクリレート、トリアリルシアヌレート等があげられる。

（発明の効果）

本発明にかかる光散乱性アクリル樹脂は、従来の常識を破る効果を有し、その高光散乱性でかつ高光透過性である点で、産業上極めて有用なものである。光散乱剤として架橋ポリマーを単独で用いると、光透過性は高いが光散乱性が不足であり、また無機物質微粉末だけでは光散乱性は高いが、光透過性が不足であるという欠点がある。本発明におけるように、架橋ポリマーと無機物質微粉末とを併用することによってこの欠点が解消できる。照明カバーのように、高光透過、高光拡散性能を要求する用途には極めて有用である。

ここでいう高光透過、高光拡散性とは、全光線透過率が80％以上、ヘーズが92％以上の性能を有するものをさす。

ここで、照明カバーに使用する場合を例にとる

と、全光線透過率が80%未満では中の電球の出力を充分大きくしないと暗く見えるので、電力エネルギーの効率的使用という点からは好ましくない。一方、ヘーズが93%未満では、中の電球のイメージがはっきり見えてしまうのでこれも都合が悪い。結局、全光線透過率が80%以上、ヘーズが93%以上であることが、照明カバー用材料として望ましい。

従来公知の材料では、いずれか一方に関して、両者を満足することはできなかった。本発明はこの不都合を解決したのである。

(実施例)

以下実施例および比較例により説明する。

実施例1

(1) 架橋ポリマーの製造

撹拌機、コンデンサーを備えた反応容器内に次の化合物を仕込んだ

メチルメタアクリレート	53部
スチレン	20部
ブチルアクリレート	16部

実施例2

(1) 架橋ポリマーの製造

下記の化合物を実施例1と同様に、撹拌機、コンデンサーを備えた反応容器内に入れて撹拌しながら80℃で3時間重合し、さらに90℃に上げて3時間重合した。その後、95℃に昇温して1時間維持した。

冷却後、脱水、乾燥してポリマー粉末を得た。得られた粉末の平均粒径は110μであった。

メチルメタアクリレート	23部
スチレン	46部
ブチルアクリレート	30部
アリルメタアクリレート	2部
n-オクチルメルカプタン	0.1部
ラウロイルパーオキサイド	2部
ポリビニルアルコール	2部
水	250部

(2) 高光透過、高光拡散性アクリル樹脂組成物の製造および評価

市販のアクリル樹脂粉末（デルパウダー

アリルメタアクリレート	1部
n-オクチルメルカプタン	0.1部
ラウロイドパーオキサイド	2部
ポリビニルアルコール	2部
水	250部

上記混合物を撹拌しながら80℃で4時間重合した。その後90℃に昇温して1時間維持した。冷却後、脱水、乾燥してポリマー粉末を得た。得られた粉末の平均粒径は100μであった。

(2) 高光透過、高光拡散性アクリル樹脂組成物の製造および評価

市販のアクリル樹脂粉末（デルパウダー80N：旭化成工業（株）製）100部に対して(1)で製造した架橋ポリマー10部と脱脂カルシウム0.9部を加えてヘンシェルミキサーで混合したあと、押出機を通してペレノイズし、これを射出成形して厚さ2mmの平板をつくった。この平板の全光線透過率は83%、ヘーズは93%であった。

80N：旭化成工業（株）製）100部に対して(1)で製造した架橋ポリマー10部と脱脂バリウム0.5部を加えてヘンシェルミキサーで混合したあと、押出機を通してペレノイズし、これを射出成形して厚さ2mmの平板をつくった。この平板の全光線透過率は83%、ヘーズは92%であった。

実施例3

実施例1でつくった架橋ポリマーを5部と脱脂カルシウム1部とをデルパウダー80Nに混合して押出機を通してペレノイズした。これを射出成形して厚さ2mmの平板をつくった。この平板の全光線透過率は80%、ヘーズは94%であった。

実施例4

実施例3で脱脂カルシウムの代りに硫酸バリウムを0.5部にした以外は同じようにして厚さ2mmの平板を得た。この平板の全光線透過率は80%、ヘーズは93%であった。

比較例1～4

架橋ポリマーと細微無機質粉末とを併用せずに、

それぞれ単独に用いた場合の例を表1に実施例とともに示す。

いずれの場合も、全光線透過率80％以上でかつ、ヘーズが93％以上という性能は得られなかつた。

表 1

	アクリル樹脂	架橋コポリマー	無機化合物	全光線透過率(%)	ヘーズ(%)
実施例1	テルポリマー100部	10部	CaCO₃ 0.9部	82	93
〃2	〃 部	10〃	BaSO₄ 0.5部	81	93
〃3	〃 部	5〃	CaCO₃ 1部	80	94
〃4	〃 部	5〃	BaSO₄ 0.5部	80	93
比較例1	〃 部	20〃	―	93	87
〃2	〃 部	20〃	―	92	88
〃3	〃 部	―	CaCO₃ 1.5部	68	94
〃4	〃 部	―	BaSO₄ 2部	62	94

特許出願人　旭化成工業株式会社

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 60-000150   (71)Applicant : ASAHI CHEM IND CO LTD

(22)Date of filing :   07.01.1985   (72)Inventor : HAYASHI MASAO

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(54) LIGHT-SCATTERING ACRYLIC RESIN COMPOSITION

(57)Abstract:

PURPOSE: The title resin composition having a high light scattering property and a high transmittance and suitable as a material for lighting covers, obtained by adding a crosslinked polymer of a specified composition to a methyl methacrylate polymer.
CONSTITUTION: 10W90wt% alkyl methacrylate in which the alkyl is of 1W4C (e.g., methyl methacrylate) is mixed with 20W40wt% aromatic vinyl monomer (e.g., styrene) and 5W50wt% alkyl acrylate in which the alkyl is of 1W8C (e.g., butyl acrylate). 100pts.wt. obtained noncrosslinking monomer mixture is copolymerized with 0.3W3pts.wt. crosslinking monomer (e.g., allyl methacrylate) to produce a crosslinked polymer of a particle diameter of 30W300μ. 1W40pts.wt. obtained crosslinked polymer is added to 100pts.wt. methyl methacrylate polymer to obtain the purpose light-scattering acrylic resin composition.

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明　細　書

1　発明の名称
　　光散乱性アクリル樹脂組成物
2　特許請求の範囲
　メチルメタクリレート系重合体100重量部に対して、下記の架橋ポリマーを1～40重量部配合して得られる光散乱性アクリル樹脂組成物
　架橋ポリマー：
　　アルキル基の炭素数1～4のアルキルメタクリレート　　　　　　　10～90重量％
　　芳香族ビニルモノマー　　20～40重量％
　　アルキル基の炭素数1～8のアルキルアクリレート　　　　　　　5～50重量％
　とから成る非架橋モノマーと、架橋性モノマー0.3～3重量％を重合して得られる粒子径30～300μの架橋ポリマー
3　発明の詳細な説明
　（産業上の利用分野）
　本発明はアクリル樹脂中に光散乱剤を分散せしめて、高い光散乱性と高い光透過性とを付与させることにより、照明カバーなどに適した光学特性を有する光散乱性アクリル樹脂組成物に関するものである。
　（従来の技術）
　光散乱性アクリル樹脂は、優雅な感覚を与えるさまざまな成形品の成形素材として賞用され、とくに照明カバーや看板用素材として賞用されている。
　照明カバー用途に用いるための光散乱性アクリル樹脂に求められる特性は、高い光散乱性を有すると同時に、高い光透過性を兼ね備えていることである。後者の特性は電力エネルギーの効率的使用の面からとくに望まれる性質である。
　光散乱性樹脂を得るためには、アクリル樹脂中に無機物質粉末を含有させることが必要とされ、これらの粉末として従来酸化チタン、硫酸バリウム、炭酸バリウム、炭酸カルシウム、二酸化ケイ素、フッ化カルシウムなどの微粉末が用いられてきた。

アリルメタクリレート 1部
n-オクチルメルカプタン 0.1部
ラウロイルパーオキサイド 2部
ポリビニルアルコール 2部
水 250部

　上記混合物を撹拌しながら80℃で4時間重合した。その後90℃に昇温して1時間保持した。冷却後、脱水・乾燥してポリマー粉末を得た。得られた粉末の平均粒径は100μであった。

(2) 高光透過・高光拡散性アクリル樹脂組成物の製造および評価
　市販のアクリル樹脂粉末（デルパウダー80N：旭化成工業㈱製）100部に対して(1)で製造した架橋ポリマーを20部加えてヘンシェルミキサーで混合したあと、押出機を通してペレタイズし、これを射出成形して厚さ2mmの平板をつくった。この平板の全光線透過率は94%、ヘーズは87%であった。

N：旭化成工業㈱製）100部に対して、(1)で製造した架橋ポリマーを30部加えてヘンシェルミキサーで混合したあと、押出機を通してペレタイズし、これを射出成形して厚さ2mmの平板をつくった。この平板の全光線透過率は91%、ヘーズは91%であった。

比較例1-3
　架橋ポリマーを用いずに、無機物質粉末を用いた場合の例を表1に実施例とともに示す。

以下余白

実施例2
(1) 架橋ポリマーの製造
　下記の化合物を実施例1と同様に、撹拌機、コンデンサーを備えた反応容器内に入れて撹拌しながら80℃で3時間重合し、さらに90℃に上げて3時間重合した。その後、95℃に昇温して1時間保持した。
　冷却後、脱水・乾燥してポリマー粉末を得た。得られた粉末の平均粒径は110μであった。

メチルメタクリレート 33部
スチレン 35部
ブチルアクリレート 30部
アリルメタクリレート 2部
n-オクチルメルカプタン 0.1部
ラウロイルパーオキサイド 2部
ポリビニルアルコール 2部
水 250部

(2) 高光透過・高光拡散性アクリル樹脂組成物の製造および評価
　市販のアクリル樹脂粉末（デルパウダー80

表 1

	アクリル樹脂	架橋コポリマー	無機化合物	全光線透過率(%)	ヘーズ(%)
実施例1	デルパウダー80N 100部	20部	-	94	87
実施例2	デルパウダー80N 100部	30部	-	91	91
比較例1	デルパウダー80N 100部	-	$CaCO_3$ 1.5部	86	94
比較例2	デルパウダー80N 100部	-	$BaSO_4$ 2部	8.2	92
比較例3	デルパウダー80N 100部	-	CaF_2 5部	73	82

Einsatzgebiete: Flaschen für kosmetische Produkte, Sprüh- und Reinigungsmittel; technische Hohlkörper; medizinische Einweggeräte, Armaturen und Verpackungsteile.

Handelsnamen z. B.: Cyrolite.

4.5.2.3 Polymethacrylimidhaltige Copolymere, PMMI

PMMI ist formal ein Copolymer aus Methylmethacrylat (MMA) und Glutaramid, wird jedoch durch die Umsetzung von PMMA mit Methylamin (MA) bei hoher Temperatur unter hohem Druck hergestellt, s. F 12.

(F 12)

PMMA   Imidierung   PMMI
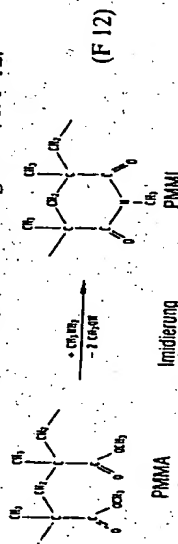
Es ist wie PMMA glasklar farblos, hat eine hohe Lichtdurchlässigkeit und keine Trübung. Der Ringschluß ergibt eine höhere Kettensteifigkeit und damit auch höhere Wärmeformbeständigkeit. Je nach Imidisierungsgrad können alle Eigenschafts-Zwischenwerte im Vergleich zum PMMA erreicht werden. PMMI hat eine geringe Sauerstoffdurchlässigkeit und ist weniger spannungsrißempfindlich gegenüber Ethanol, Ethanol/Wasser- und Isooctan/Toluol-Gemischen.

Die Verarbeitung im Spritzguß erfolgt nach Vortrocknung des Granulats bei 140°C bei Massetemperaturen von 200 bis 310°C und Werkzeugtemperaturen von 120 bis 150°C.

Eigenschaftsvergleich s. Tafel 4.22

Einsatzgebiete: Scheinwerfer-Streulichtscheiben für Kfz, Straßenleuchten-Abdeckungen, als Blendkomponente und als faserverstärkter Konstruktionswerkstoff. PMMI-Schaum s. Abschn. 4.10.2.4.

Handelsnamen z. B.: Pleximid, Kamax, PMI-Resin.

4.5.2.4 Schlagzähe PMMA

Schlagzähe Formmassen werden durch die Suspensions- oder Emulsionspolymerisation zweiphasig hergestellt. In der PMMA-Matrix bilden z. B. mit Styrol modifizierte Acrylat-Elastomere ($\leq$30 %, im Brechungsindex angeglichen) die zähmachende disperse Phase. Durch diesen Aufbau sind Formstoffe aus den uneingeschränkt mit PMMA mischbaren schlagzähen Massen in gleicher Weise witerungsstabil und glasklar wie reines PMMA. Ihre Spannungsrißempfindlichkeit ist geringer, ihre Heißwasser-Beständigkeit besser.

Die Verarbeitung erfolgt nach Vortrocknung oder mit Entgasungsschnecken im Spritzguß und durch Extrusion bei Massetemperaturen von 210 bis 230°C und Werkzeugtemperaturen von 60 bis 80°C.

Eigenschaftsvergleich s. Tafel 4.22

Einsatzgebiete: Witerungsschutzschicht bei Bauprofilen wie z. B. PVC-Fensterprofile, Haushalts-, Zeichen- und Schreibgeräte; Sanitärteile, Leuchtenabdeckungen.

Handelsnamen z. B.: Diakon, Lucryl, Oroglas, Plexiglas.

4.5.2.5 PMMA+ABS

Ein Blend dieser Art findet für Kfz-Teile (Gehäuse, Reflektoren) sowie im Apparatebau und der Elektroindustrie Anwendung. Das Material ist metallisierbar, zeigt gutes Schweißverhalten und besitzt eine bessere Witterungsbeständigkeit und Steifigkeit als ABS.

Handelsname: Plexalloy

4.5.2.6 Spezialprodukte, Polyacrylat-Harze (Handelsnamen in Klammern)

Homopolymere *Acrylsäureester* (PAA) sind weiche Harze, deren Bedeutung wegen ihrer guten Beständigkeit gegen Licht, oxidative Einflüsse und Wärme und ihrer elastifizierenden Wirkung in der Co- und Terpolymerisation mit PS, PVC, VA, MA, AN und Acrylsäure liegt. Diese werden als Festharze oder Lösungen, hauptsächlich aber als Dispersionen geliefert (Acronal, Acrysol, Plexigum, Plexisol). *Oxalidin-modifizierte Acryllack-Harze* (Acryloid) sind mit Isocyanaten vernetzbar. *Elastoplastische Copolymerisate* sind Grundstoffe für Fugendichtungsmassen, solche mit >20% Acrylsäure sind wasserlöslich. *Polyhydroxyethyl-methacrylat* (Hydron) wird mit ca. 40% Wasser gesättigt für Kontaktlinsen und zur Beschichtung (z. B. von Brillen) und Umhüllungen mit kontrollierten Wasser-Aufnahmen und -Durchlässigkeiten in der Medizin und Technik, eingesetzt. Im Verdauungstrakt *lösliche Acrylharze* (Endragit) braucht man zur Umhüllung von Medikamenten. Durch Einpolymerisieren untereinander oder mit Zweitkomponenten (z. B. Isocyanaten) *vernetzbarer* Komponenten stellt man heiß- oder strahlenhärtbare Lackharze her (z. B. Acryplex, Degalan, Larodur, Macrynal, Plex, Scopacron, Synthacryl). Hart eingestellte *Methacrylat-Copolymerisate* verwendet man als Schlußstrich für Kunstleder und andere treibstoffbeständige Lackierungen. *MMA-VC-Copolymere* (z. B. Paraloid) sind Elastifikatoren für PVC. Ungesättigte aliphatische Polyurethan-Acrylatharze (Crestomer) sind mit H_2O_2 vernetzbare, zähe, flexible GFK-Laminierharze.

4.6 Polyacetale, POM

4.6.1 Generelle Beschreibung

POM (Polyoxymethylen, Polyformaldehyd, Polyacetale) sind teilkristalline Thermoplaste, die durch Homo- (POM-H) oder Copolymerisation (POM-R) von Formaldehyd entstehen, s. F 13.

POLYMER HANDBOOK

SECOND EDITION

J. BRANDRUP • E. H. IMMERGUT, Editors

with the collaboration of

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REFRACTIVE INDICES OF POLYMERS

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The table presents the refractive indices of polymers in order of increasing n_D. It contains mainly homopolymers but a few copolymers of special technical interest have been included. Temperatures are in $^{\circ}C$.

The following general remarks may be helpful for the calculation of approximate refractive indices of other polymers and copolymers.

Calculation of Refractive Indices

The Lorentz-Lorenz Equation

$$(n^2 - 1)/(n^2 + 2) = R/M \, \rho = r \rho \qquad (1)$$

correlates the refractive index n to the density ρ, the molecular weight M and the molar refractivity R, where $R/M = r$ is the specific refractivity. It seems to be reasonable to assume that the molar refractivity R of a polymer molecule is the sum of the molar refractivities of the monomer subunits R_M, i. e. $R = DP \, R_M$, where DP is the degree of polymerization. With $M = DP \cdot M_M$ (M_M = molecular weight of the monomer unit) the Lorentz-Lorenz Equation for polymers may be written

$$(n^2 - 1)/(n^2 + 2) = R_M/M_M \, \rho = r_M \rho \qquad (2)$$

containing only the refractivity of the repeating unit.

Using incremental atomic or bond refractivities (1 –4) the refractive indices of various kinds of polymers have been calculated according to the above Equation (1) to give fairly good agreement with measured values.

Refractive Indices of Copolymers (Monomer A and B)

If only the refractive indices n_A and n_B of the corresponding homopolymers are known, a rough estimation of the refractive index n_{AB} of a random copolymer may be obtained by interpolation with respect to the composition by weight (5): $n_{AB} = c_A n_A + (1 - c_A) n_B$.

A more exact calculation is possible, if the densities ρ_A and ρ_B of the homopolymers as well as the density ρ_{AB} of the copolymer are known. It is advisable to calculate first the specific refractivities r_A and r_B from n_A, ρ_A and n_B, ρ_B by use of the Lorentz-Lorenz Equation. By interpolation with regard to the weight contents $r_{AB} = c_A r_A + (1 - c_A) r_B$ is obtained. With this r_{AB} and the known density ρ_{AB} the Lorentz-Lorenz Equation gives a fairly accurate refractive index n_{AB}.

The calculation methods described are applicable in the same way to multi-phase systems like blends, block or graft copolymers or partially crystalline polymers, if the phase dimensions are well below the wavelength of light.

Temperature Dependence (dn/dT)

From the Lorentz-Lorenz Equation the following expression can easily be derived:

$$\frac{dn}{dT} = \frac{(n^2 + 2)(n^2 - 1)}{6n} \cdot \frac{1}{\rho}\frac{d\rho}{dT} = -q(n)\alpha \qquad (3)$$

where $\alpha = -d\rho/\rho dT$ is the thermal expansion coefficient. $q(n)$ increases from 0.46 ($n = 1.4$) to 0.59 ($n = 1.5$) to 0.74 ($n = 1.6$) in the refractive index range of interest for polymers. With $\alpha = 1.5 \ldots 2.5 \times 10^{-4}/^{\circ}C$ for hard polymers below their glass transition temperature and $\alpha = 5 \ldots 7 \times 10^{-4}/^{\circ}C$ for amorphous polymers above their glass transition temperature the following rough approximation may be obtained:

$$-dn/dT = 1 \ldots 2 \times 10^{-4}/^{\circ}C \quad \text{for glassy polymers,}$$
$$-dn/dT = 3 \ldots 5 \times 10^{-4}/^{\circ}C \quad \text{for amorphous polymers above the glass transition.}$$

Partially crystalline polymers which are ductile in character like polyolefins, aliphatic polyesters and cellulosic resins, have intermediate values.

Influence of Molecular Weight

End-group refractivities are always more or less different from the refractivity of the repeating unit of the chain. Therefore the refractive index of the whole polymer may strongly depend on the chain length at very low degrees of polymerization. Knowing the refractivities of end-group and repeating unit the degree of polymerization can be obtained from the refractive index (5). In polymers with more than 500 to 1000 chain atoms the refractive index has approached a limiting value (5).

Polymer	n_D	$T\,^{\circ}C$	Polymer	n_D	$T\,^{\circ}C$
Poly(tetrafluoroethylene-co-hexafluoropropylene)	1.338		Poly(heptafluorobutyl acrylate)	1.367	25
Poly(pentadecafluorooctyl acrylate)	1.339	25	Poly(trifluorovinyl acetate)	1.375	25
Poly(tetrafluoro-3-(heptafluoropropoxy)propyl acrylate)	1.346	25	Poly(octafluoropentyl acrylate)	1.380	25
			Poly(pentafluoropropyl acrylate)	1.385	25
Poly(tetrafluoro-3-(pentafluoroethoxy)propyl acrylate)	1.348	25	Poly(2-(heptafluorobutoxy)ethyl acrylate)	1.390	25
			Poly(2,2,3,4,4,4-hexafluorobutyl acrylate)	1.392	25
Poly(tetrafluoroethylene)	1.35	(-1.38)	Poly(trifluoroethyl acrylate)	1.407	25
Poly(undecafluorohexyl acrylate)	1.356		Poly(2-(1,1,2,2-tetrafluoroethoxy)ethyl acrylate)	1.412	25
Poly(nonafluoropentyl acrylate)	1.360	25	Poly(trifluoroisopropyl methacrylate)	1.4177	20
Poly(tetrafluoro-3-(trifluoromethoxy)propyl acrylate)	1.360	25	Poly(2,2,2-trifluoro-1-methylethyl methacrylate)	1.4185	
			Poly(2-(trifluoroethoxy)ethyl acrylate)	1.419	25
Poly(pentafluorovinyl propionate)	1.364	25	Poly(trifluorochloroethylene)	1.42-1.43	

REFRACTIVE INDICES

Polymer	n_D	$T\,^{\circ}C$
Poly(vinylidene fluoride)	1.42	25
Poly(dimethylsilylene) (poly(dimethyl siloxane))	1.43	
Poly(trifluoroethyl methacrylate)	1.437	
Poly(oxypropylene)	1.4495	
Poly(vinyl isobutyl ether)	1.4507	30
Poly(vinyl ethyl ether)	1.4540	30
Poly(oxyethylene)	1.4563	30
Poly(vinyl butyl ether)	1.4563	30
Poly(vinyl pentyl ether)	1.4581	30
Poly(vinyl hexyl ether)	1.4591	30
Poly(4-methyl-1-pentene)	1.459-1.465	
Cellulose acetate butyrate	1.46-1.49	
Poly(4-fluoro-2-trifluoromethylstyrene)	1.46	
Poly(vinyl octyl ether)	1.4613	30
Poly(vinyl 2-ethylhexyl ether)	1.4626	30
Poly(vinyl decyl ether)	1.4628	30
Poly(2-methoxyethyl acrylate)	1.463	25
Poly(butyl acrylate)	1.4631	30
Poly(butyl acrylate)	1.466	20
Poly(tert-butyl methacrylate)	1.4638	20
Poly(vinyl dodecyl ether)	1.4640	30
Poly(3-ethoxypropyl acrylate)	1.465	25
Poly(oxycarbonyl tetramethylene)	1.465	50
Poly(vinyl propionate)	1.4665	20
Poly(vinyl acetate)	1.4665	20
Poly(vinyl methyl ether)	1.467	20
Poly(ethyl acrylate)	1.4685	20
Poly(ethylene-co-vinyl acetate)	1.47-1.50	
(80% - 20% vinyl acetate)		
Cellulose propionate	1.47-1.49	
Cellulose acetate propionate	1.47	
Benzyl cellulose	1.47-1.58	
Phenol-formaldehyde resins	1.47-1.70	
Cellulose triacetate	1.47-1.48	
Poly(vinyl methyl ether) (isotactic)	1.4700	30
Poly(3-methoxypropyl acrylate)	1.471	25
Poly(2-ethoxyethyl acrylate)	1.471	25
Poly(methyl acrylate)	1.472-1.480	
Poly(isopropyl methacrylate)	1.4728	20
Poly(1-decene)	1.4730	
Poly(propylene) (atactic, density 0.8575 g/cm^3)	1.4735	20
Poly(vinyl sec-butyl ether) (isotactic)	1.4740	30
Poly(dodecyl methacrylate)	1.4740	20
Poly(oxyethyleneoxysuccinoyl)	1.4744	25
(poly(ethylene succinate)).		
Poly(tetradecyl methacrylate)	1.4746	30
Poly(ethylene-co-propylene) (EPR-rubber)	1.4748-1.48	
Poly(hexadecyl methacrylate)	1.4750	30
Poly(vinyl formate)	1.4757	20
Poly(2-fluoroethyl methacrylate)	1.4768	20
Poly(isobutyl methacrylate)	1.477	20
Ethyl cellulose	1.479	21
Poly(vinyl acetal)	1.48-1.50	
Cellulose acetate	1.48-1.50	
Cellulose tripropionate	1.48-1.49	
Poly(oxymethylene)	1.48	20
Poly(vinyl butyral)	1.48-1.49	
Poly(n-hexyl methacrylate)	1.4813	20
Poly(n-butyl methacrylate)	1.483	20-25
Poly(ethylidene dimethacrylate)	1.4831	20
Poly(2-ethoxyethyl methacrylate)	1.4833	20
Poly(oxyethyleneoxymaleoyl)	1.4840	25
(poly(ethylene maleate))		
Poly(n-propyl methacrylate)	1.484	25
Poly(3,3,5-trimethylcyclohexyl methacrylate)	1.485	20
Poly(ethyl methacrylate)	1.485	20-25
Poly(2-nitro-2-methylpropyl methacrylate)	1.4868	20
Poly(triethylcarbinyl methacrylate)	1.4889	20
Poly(1,1-diethylpropyl methacrylate)	1.4889	20
Poly(methyl methacrylate)	1.4893	23
Poly(2-decyl-1,3-butadiene)	1.490	20
Poly(vinyl alcohol)	1.4899	20.5
Poly(ethyl glycolate methacrylate)	1.49-1.53	
Poly(3-methylcyclohexyl methacrylate)	1.4903	20
Poly(cyclohexyl α-ethoxyacrylate)	1.4947	20
Methyl cellulose (low viscosity)	1.4969	20
Poly(4-methylcyclohexyl methacrylate)	1.497	25
Poly(decamethylene glycol dimethacrylate)	1.4975	20
Poly(urethanes)	1.4990	
Poly(1,2-butadiene)	1.5-1.6	
Poly(vinyl formal)	1.5000	20
Poly(2-bromo-4-trifluoromethylstyrene)	1.50	
Cellulose nitrate	1.5	25
Poly(sec-butyl α-chloroacrylate)	1.50-1.514	
Poly(2-heptyl-1,3-butadiene)	1.500	25
Poly(ethyl α-chloroacrylate)	1.5000	
Poly(2-isopropyl-1,3-butadiene)	1.502	25
Poly(2-methylcyclohexyl methacrylate)	1.5028	30
Poly(propylene) (density 0.9075 g/cm^3)	1.5028	20
Poly(isobutene)	1.5030	20
Poly(bornyl methacrylate)	1.505-1.51	
Poly(2-tert-butyl-1,3-butadiene)	1.5059	20
Poly(ethylene glycol dimethacrylate)	1.5060	24.6
Poly(cyclohexyl methacrylate)	1.5063	20
Poly(cyclohexanediol-1,4-dimethacrylate)	1.5066	20
Butyl rubber (unvulcanized)	1.5067	20
Poly(tetrahydrofurfuryl methacrylate)	1.508	
Gutta percha (β)	1.5096	20
Poly(ethylene) Ionomer	1.509	
Poly(oxyethylene) (high molecular weight)	1.51	
Poly(ethylene) (density 0.914 g/cm^3)	1.51-1.54	
--, (density 0.94-0.945 g/cm^3)	1.51	20
--, (density 0.965 g/cm^3)	1.52-1.53	20
Poly(1-methylcyclohexyl methacrylate)	1.545	20
Poly(2-hydroxyethyl methacrylate)	1.5111	20
Poly(vinyl chloroacetate)	1.5119	20
Poly(butene) (isotactic)	1.512	25
Poly(vinyl methacrylate)	1.5125	
Poly(N-butyl methacrylamide)	1.5129	20
Gutta percha (α)	1.5135	20
Terpene resin	1.514	50
Poly(1,3-butadiene)	1.515	25
Shellac	1.5154	25
Poly(methyl α-chloroacrylate)	1.51-1.53	
Poly(2-chloroethyl methacrylate)	1.517	20
Poly(2-diethylaminoethyl methacrylate)	1.517	20
Poly(2-chlorocyclohexyl methacrylate)	1.5174	20
Poly(1,3-butadiene) (35% cis; 56% trans; 7% 1,2-content)	1.5179	20
Natural rubber	1.5180	
Poly(allyl methacrylate)	1.519-1.52	
Poly(vinyl chloride) + 40% dioctyl phthalate	1.5196	20
Poly(acrylonitrile)	1.52	
	1.52	
Poly(methacrylonitrile)	1.5187	25
Poly(1,3-butadiene) (high cis-type)	1.52	
Poly(butadiene-co-acrylonitrile)	1.52	
	1.52	

Polymer	n_D	T°C
Poly(methyl isopropenyl ketone)	1.5200	20
Poly(isoprene)	1.521	20
Poly(ester) resin, rigid (ca. 50 % styrene)	1.523-1.54	
Poly(N-(2-methoxyethyl)methacrylamide)	1.5246	20
Poly(2,3-dimethylbutadiene) (methyl rubber)	1.525	
Poly(vinyl chloride-co-vinyl acetate) (95/5-90/10)	1.525-1.535	
Poly(acrylic acid)	1.527	25
Poly(1,3-dichloropropyl methacrylate)	1.5270	20
Poly(2-chloro-1-(chloromethyl)ethyl methacrylate)	1.5270	20
Poly(acrolein)	1.529	
Poly(1-vinyl-2-pyrrolidone)	1.53	
Hydrochlorinated rubber	1.53-1.55	
Nylon 6; Nylon 6,6; Nylon 6,10 (moulding)	1.53	
(Nylon-6-fiber: 1.515 transverse, 1.565 in fiber direction)		
Poly(butadiene-co-styrene) (ca. 30 % styrene) black copolymer	1.53	
Poly(cyclohexyl α-chloroacrylate)	1.532	25
Poly(2-chloroethyl α-chloroacrylate)	1.533	25
Poly(butadiene-co-styrene) (ca. 75/25)	1.535	
Poly(2-aminoethyl methacrylate)	1.537	20
Poly(furfuryl methacrylate)	1.5381	
Proteins	1.539-1.541	
Poly(butylmercaptyl methacrylate)	1.5390	20
Poly(1-phenyl-n-amyl methacrylate)	1.5396	20
Poly(N-methyl-methacrylamide)	1.5388	20
Cellulose	1.54	
Poly(vinyl chloride)	1.54-1.55	
Urea formaldehyde resin	1.54-1.56	
Poly(sec-butyl α-bromoacrylate)	1.542	25
Poly(cyclohexyl α-bromoacrylate)	1.542	25
Poly(2-bromoethyl methacrylate)	1.5426	20
Poly(dihydroabietic acid)	1.544	
Poly(abietic acid)	1.546	25
Poly(ethylmercaptyl methacrylate)	1.547	20
Poly(N-allyl methacrylamide)	1.5476	20
Poly(1-phenylethyl methacrylate)	1.5487	20
Poly(vinylfuran)	1.55	20
Poly(2-vinyltetrahydrofuran)	1.55	20
Poly(vinyl chloride) + 40 % tricresyl phosphate	1.55	
Epoxy resins	1.55-1.60	
Poly(p-methoxybenzyl methacrylate)	1.552	20
Poly(isopropyl methacrylate)	1.552	
Poly(p-isopropylstyrene)	1.554	20
Poly(chloroprene)	1.554-1.558	
Poly(oxyethylene)-α-benzoate-ω-methacrylate)	1.555	20
Poly(p,p'-xylylenyl dimethacrylate)	1.5559	20
Poly(1-phenylallyl methacrylate)	1.5573	20
Poly(p-cyclohexylphenyl methacrylate)	1.5575	20
Poly(2-phenylethyl methacrylate)	1.5592	20
Poly(oxycarbonyloxy-1,4-phenylene-1-propyl-butylidene-1,4-phenylene)	1.5602	
Poly(1-(o-chlorophenyl)ethyl methacrylate)	1.5624	20
Poly(styrene-co-maleic anhydride)	1.564	21
Poly(1-phenylcyclohexyl methacrylate)	1.5645	20
Poly(oxycarbonyloxy-1,4-phenylene-1,3-dimethyl-butylidene-1,4-phenylene)	1.5671	
Poly(methyl α-bromoacrylate)	1.5672	20
Poly(benzyl methacrylate)	1.5680	20
Poly(2-(phenylsulfonyl)ethyl methacrylate)	1.5682	
Poly(m-cresyl methacrylate)	1.5683	20
Poly(styrene-co-acrylonitrile) (ca. 75/25)	1.57	
Poly(oxycarbonyloxy-1,4-phenyleneisobutylidene-1,4-phenylene)	1.5702	

Polymer	n_D	T°C
Poly(o-methoxyphenyl methacrylate)	1.5705	20
Poly(phenyl methacrylate)	1.5706	20
Poly(o-cresyl methacrylate)	1.5707	20
Poly(diallyl phthalate)	1.572	20
Poly(2,3-dibromopropyl methacrylate)	1.5739	20
Poly(oxycarbonyloxy-1,4-phenylene-1-methyl-butylidene-1,4-phenylene)	1.5745	
Poly(oxy-2,6-dimethylphenylene)	1.575	
Poly(oxyethyleneoxyterephthaloyl) (amorphous) (poly(ethylene terephthalate)) (crystalline fiber: 1.51 transverse; 1.64 in fiber direction)	1.5750	20
Poly(vinyl benzoate)	1.5775	20
Poly(oxycarbonyloxy-1,4-phenylenebutylidene-1,4-phenylene)	1.5792	
Poly(1,2-diphenylethyl methacrylate)	1.5816	20
Poly(o-chlorobenzyl methacrylate)	1.5823	20
Poly(oxycarbonyloxy-1,4-phenylene-sec-butylidene-1,4-phenylene)	1.5827	
Poly(oxypentaerythritoloxyphthaloyl)	1.584	20
Poly(m-nitrobenzyl methacrylate)	1.5845	20
Poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)	1.5850	
Poly(N-(2-phenylethyl)methacrylamide)	1.5857	20
Poly(4-methoxy-2-methylstyrene)	1.5868	20
Poly(o-methylstyrene)	1.5874	20
Poly(styrene)	1.59-1.592	20
Poly(oxycarbonyloxy-1,4-phenylenecyclohexylidene-1,4-phenylene)	1.5900	
Poly(o-methoxystyrene)	1.5932	20
Poly(diphenylmethyl methacrylate)	1.5933	20
Poly(oxycarbonyloxy-1,4-phenyleneethylidene-1,4-phenylene)	1.5937	
Poly(p-bromophenyl methacrylate)	1.5964	20
Poly(N-benzyl methacrylamide)	1.5965	20
Poly(p-methoxystyrene)	1.5967	20
Hard rubber (32 % S)	1.6	
Poly(vinylidene chloride)	1.60-1.63	
Poly(sulfides) ("Thiokol")	1.6-1.7	
Poly(o-chlorodiphenylmethyl methacrylate)	1.6040	20
Poly(oxycarbonyloxy-1,4-(2,6-dichloro)phenylene-isopropylidene-1,4-(2,6-dichloro)phenylene))	1.6056	
Poly(oxycarbonyloxybis(1,4-(3,5-dichlorophenylene))	1.6056	
Poly(pentachlorophenyl methacrylate)	1.608	20
Poly(o-chlorostyrene)	1.6098	20
Poly(phenyl α-bromoacrylate)	1.612	25
Poly(p-divinylbenzene)	1.6150	20
Poly(N-vinylphthalimide)	1.6200	20
Poly(2,6-dichlorostyrene)	1.6248	20
Poly(β-naphthyl methacrylate)	1.6298	20
Poly(α-naphthyl carbinyl methacrylate)	1.63	
Poly(sulfone)	1.633	
Poly(2-vinylthiophene)	1.6376	20
Poly(α-naphthyl methacrylate)	1.6410	20
Poly(oxycarbonyloxy-1,4-phenylenediphenyl-methylene-1,4-phenylene)	1.6539	
Poly(vinyl phenyl sulfide)	1.6568	20
Butylphenol formaldehyde resin	1.66	
Urea-thiourea-formaldehyde resin	1.660	25
Poly(vinylnaphthalene)	1.6818	20
Poly(vinylcarbazole)	1.683	20
Naphthalene-formaldehyde resin	1.696	
Phenol-formaldehyde resin	1.70	
Poly(pentabromophenyl methacrylate)	1.71	20

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Document D12

POLYMER BLENDS

Volume 2: Performance

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Contents

timum particle-size ranges
i two exceptions involving
is found between 0.2 and
n has been observed [66].
; manufacturers to set their
litions when melt blended
im particle size for a given
iavior of core-shell parti-
ew experimental facts are
iese ranges for core-shell
ir core-shell particles un-
purely scientific reasons.
'ying them, that optimum
ind PC-PET blends with
:al agreement with results
: that certain properties of
i complicate this analysis
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at T_g in the polymer core
letermine the quality of
icles, rubber cores with
ig at lower temperatures
performing modifiers is
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g core-shell polymers in
e low surface tension of
iers and polymers gener-
ppear to have been over-
fetablen ^{TM}S-2001 [69],
:e prepared by polymer-
e-based latex, prepared
.e latex particles to help
ire 24.11 shows that the
licone provide the most
silicone moiety in these
s to increase. However,
modifiers (AIMS) and
their superior weather-
].

/ available PMMA or
ieed to use alternative
shell particles in these

Figure 24.11 Toughening of PVC with a silicone-containing butyl acrylate core-shell parti-
cle. About 50% of silicone rubber in the core produces optimum results. See [69]. Reproduced
with permission from the publisher.

types of polymers. The most well-known method is to take advantage of the end
groups present in engineering polymers. Amine and carboxyl groups in nylons and
carboxyl and hydroxyl groups in polyesters offer potentially reactive sites for suit-
able chemical moieties placed on the shell. Functional monomers, such as acrylic
and methacrylic acids, glycidyl methacrylate (GMA), hydroxyethyl acrylate (HEA)
or methacrylate (HEMA), and maleic anhydride (MAH), have been used to induce
chemical adhesion with the matrix in this fashion [72, 73]. The incorporation of
these types of monomers into the shell via emulsion polymerization is not trivial,
because their high water solubility hinders chemical bonding to the shell during
polymerization. Another option for enhancing the adhesion between the matrix and
the shell is to add a compatibilizing agent, which is a well-documented method.
(See Chapter 17.)

4. *Microstructural Variants* Significant examples of these variants, which have
been available commercially for some time, are the multilayer particles used to
toughen PMMA [7, 74, 75]. These particles provide an optimum balance of stiffness
and impact resistance. Attempts at using more sophisticated types of morphology
inside the rubber cores, such as interpenetrating polymer networks (IPN) of two soft
polymers with different T_g's, are also interesting, although their performance in early
experiments is similar to that of typical core-shell polymers [76].

B. Toughening of Thermoplastic Matrices

1. *Poly(Methyl Methacrylate)* Rubber-toughened PMMA (RT-PMMA) has been
the focus of commercial and scientific interest for many years [7, 75, 77-80]. Besides

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TOUGHE

3LA　　3LAI　　3LAII　　4L

2L　　3LB　　3LC　　3LD　　3LE
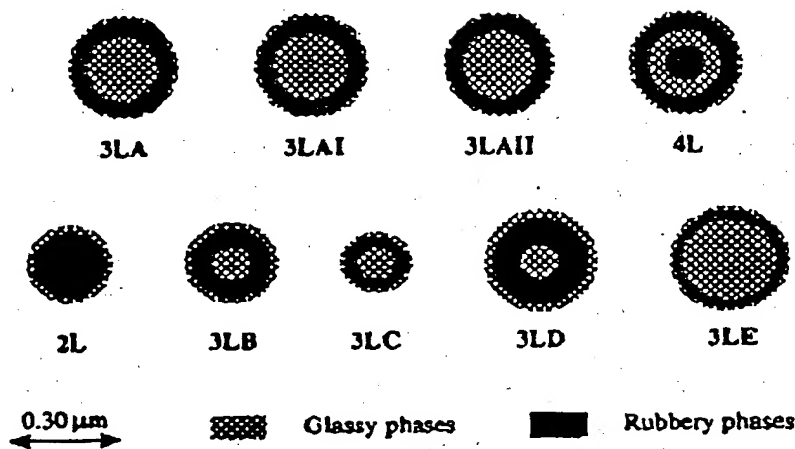
0.30 μm　　▨▨ Glassy phases　　█ Rubbery phases

Figure 24.12　Multilayer structures that combine glassy and rubbery phases in different sequences and distributions. Particles 3LE, with one glassy phase at the center and one on the outside, provide an optimum balance between toughness and stiffness. From [79], with permission from the publisher.

improving the fracture resistance of the polymer, core–shell modifiers for PMMA must also maintain the high stiffness of the matrix as well as its clarity. For that reason, suitable combinations of butyl acrylate and styrene monomers are used in the rubbery phase, while a PMMA copolymer is used in the glassy phase, to match the refractive index of the matrix. Particles on the order of 0.2 to 0.3 μm are normally used. The level of modifier particles present can vary from 10 to 40% by weight of the matrix. In commercial materials, optimum toughening is obtained with a multi-layer particle morphology that consists either of a rubbery core and a glassy shell or a glassy core, an intermediate rubbery layer, and an outer glassy shell [7, 79]. In general, RT-PMMA is sold commercially as a final blend, as with HIPS and ABS resins. Figure 24.6 is an atomic force micrograph that clearly shows the typical microstructure of RT-PMMA.

Lovell, Young, and collaborators carried out a detailed study of how different sequences of multilayer structures offer different degrees of ductility in PMMA while maintaining stiffness and clarity [81, 82]. Figure 24.12 shows schematic diagrams of cross sections of the types of particles used by these authors to toughen PMMA. The decrease in elastic modulus depends on the amount of rubber present in the modifier and not on the sequence of hard and soft layers. An optimum balance between stiffness and impact was obtained for the particles with a hard core and hard shell, with an intermediate rubber layer, as shown in Fig. 24.13.

2. *Poly(Vinyl Chloride)*　The miscibility of poly(vinyl chloride) (PVC) with PMMA, a common type of shell in commercial modifiers, is a driving force that facilitates dispersion and promotes adhesion between the particles and the matrix.
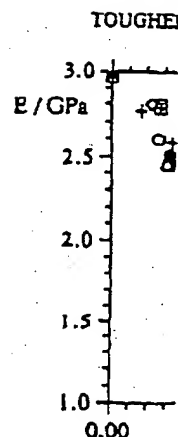
E / GPa

3.0
2.5
2.0
1.5
1.0
0.00

Figure 24.13　Your ber-toughened PMM. fraction of the modif concentration. Repro

Lutz and Dunkelbe tion of PVC [1].

The degree of i processing and fo: Chapter 18) and make a difference Chapter 1 in [1].) .

Typical levels o: parts per hundred (; typical of various p core–shell polymer an MBS modifier [decreases), neat PV modified with the very sharp notches

All-acrylic imp: for which weather Methacrylate-butac quired, as, for exa (1.564) and its esse: binations of mono: small particle size :

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(54)【発明の名称】　光拡散性樹脂

(57)【要約】
【構成】　実質的に透明な樹脂中に、平均粒径が1〜30
μmの範囲内であり、粒径分布の標準偏差がその平均粒
径の20％以下である架橋重合体微粒子を分散せしめてな
る光拡散性樹脂。
【効果】　この光拡散性樹脂は，高い光散乱性及び光線
透過率を併せ持ち、照明カバー、ディスプレー、照明看
板等に好適に利用できる。

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1

【特許請求の範囲】
【請求項1】　実質的に透明な樹脂中に、平均粒径が1
～30μmの範囲内であり、粒径分布の標準偏差がその平
均粒径の20％以下である架橋重合体微粒子を分散せしめ
てなる光拡散性樹脂。
【請求項2】　実質的に透明な樹脂が、メタクリル系樹
脂ポリスチレン樹脂、ポリカーボネート樹脂、エポキシ
樹脂及びポリ塩化ビニル樹脂から選ばれる少なくとも1
種を主成分とする樹脂である請求項1記載の光拡散性樹
脂。
【請求項3】　架橋重合体微粒子が、（メタ）アクリル
酸メチル及び／又はスチレンと多官能（メタ）アクリ
レートとの共重合体である請求項1記載の光拡散性樹脂。
【発明の詳細な説明】
【0001】
【産業上の利用分野】本発明は、各種ディスプレイ、照
明看板、透過型スクリーン、照明カバー等の光拡散機能
の求められる材料に好適に用いられる光拡散性樹脂に関
する。
【0002】
【従来の技術及び発明が解決しようとする課題】従来、
照明カバー、スクリーン等に用いられる光拡散性材料と
しては、透明プラスチックに有機又は無機の微粒子を分
散させた材料が知られている。これらの材料に求められ
る性能としては、均一にかつできるだけ広い範囲に光を
拡散させる事が重要である。ところが、光源から出る光
量は一定であるため、最も好ましい輝度と広がりを得る
べく、光拡散材の濃度、粒径等を変えることにより最適
化を図っているのが現状である。さらに、光拡散材であ
る微粒子と樹脂との屈折率の差を指標として種々の材料
が提案されている。しかしながら、高散乱性が要求され
るリアプロジェクションテレビ用のスクリーン、エレク
トロルミネッセンス（EL）用の光拡散基材等の用途に
おいても十分に満足すべき光拡散性を有する光拡散性材
料は存しなかった。
【0003】
【課題を解決するための手段】かかる実状において、本
発明者らは優れた光拡散性材料を得るべく鋭意検討を重
ねた結果、樹脂中に分散する微粒子の粒径分布が光拡散
性能を左右する重要な因子であり、粒径分布を一定範囲
内とすれば、優れた光拡散性能を有し、かつ透過光が着
色しない光拡散性樹脂が得られることを見出し、本発明
を完成した。
【0004】すなわち、本発明は実質的に透明な樹脂中
に、平均粒径が1～30μmの範囲内であり、粒径分布の
標準偏差がその平均粒径の20％以下である架橋重合体微
粒子を分散せしめてなる光拡散性樹脂を提供するもので
ある。
【0005】本発明に用いられる架橋重合体微粒子の平
均粒径は、1～30μmの範囲、好ましくは2～15μmの

</div>

2

範囲である。平均粒径が1μm未満であると透過光が着
色するために好ましくなく、また30μmを超えると透過
光の散乱強度が低下する傾向にあるため不都合が生じ
る。
【0006】本発明においては当該架橋重合体微粒子の
粒径分布の標準偏差がその平均粒径の20％以下、即ち、
単分散性の高い微粒子であることが必要である。当該標
準偏差が20％を超える場合、即ち、多分散の微粒子で
は、光散乱性と光透過性の両者を充分満足できない。
【0007】また、架橋重合体微粒子の形状は、特に限
定されるものではないが、真球状が好ましい。なお、微
粒子の表面は多孔質であってもよい。
【0008】かかる一定範囲の平均粒径と粒径分布を有
する架橋重合体微粒子は、例えば懸濁重合法を用いて得
た架橋重合体微粒子に分級処理を施して粒径を揃えても
よいし、またいわゆるシード重合法を用いて粒径の揃っ
た架橋重合体微粒子を製造してもよい。
【0009】本発明に使用される架橋重合体微粒子を構
成する重合体としては、特に制限されるものではない
が、スチレン／ジビニルベンゼン、スチレン／エチレン
グリコールジメタクリレート、スチレン／ブタジエン等
のスチレン系架橋共重合体；メチル（メタ）アクリレー
ト／ジビニルベンゼン、メチル（メタ）アクリレート／
エチレングリコールジメタクリレート、メチル（メタ）
アクリレート／メチレンビスアクリルアミド等の（メ
タ）アクリル酸エステル系架橋共重合体；エチレン／ブ
タジエン、メチルビニルエーテル／ジビニロキシブタ
ン、酢酸ビニル／ジビニロキシブタン、塩化ビニル／ジ
ビニルベンゼン等のオレフィン系架橋共重合体等が挙げ
られる。なお、メタクリル樹脂を基体として用いる場合
には、メチルメタクリレート及び／又はスチレンと多官
能（メタ）アクリレートとを共重合することにより得ら
れる微粒子が好適に用いられる。ここで多官能（メタ）
アクリレートとしては、エチレングリコールジ（メタ）
アクリレート、ジエチレングリコールジ（メタ）アクリ
レート、テトラエチレングリコールジ（メタ）アクリ
レート等の（ポリ）エチレングリコールジ（メタ）アクリ
レート；プロピレングリコールジ（メタ）アクリレー
ト、1，3－ブタンジオールジ（メタ）アクリレート、
テトラエチレングリコールジ（メタ）アクリレート、ネ
オペンチルグリコールジ（メタ）アクリレート等のグリ
コールジ（メタ）アクリレート；トリメチロールプロパ
ントリ（メタ）アクリレート、ペンタエリスリトールテ
トラ（メタ）アクリレート等の多価アルコールの（メ
タ）アクリレート類等が使用される。
【0010】光拡散性樹脂の基体樹脂としては、実質的
に透明な樹脂であることが必要であるが、透明性（光透
過率）が高いものほど好ましい。この様な樹脂として
は、メタクリル樹脂、エポキシ樹脂、ポリカーボネート
樹脂、ポリスチレン樹脂、ポリ塩化ビニル樹脂等が使用

3

される。

【0011】本発明の光拡散性樹脂を製造する方法としては、例えば前記の架橋重合体微粒子を重合性単量体もしくは部分重合した重合性モノマーのシラップ中に分散させて重合するか、又は、架橋重合体微粒子と予め調製した基体用樹脂とを溶融混練してプレスする方法が挙げられる。また、光拡散性樹脂を、薄膜状のフィルムに成形したい場合には、スクリーン印刷等の方法を用いることもできる。

【0012】光拡散性樹脂中への架橋重合体微粒子の配合割合は、1～10重量％が好ましい。微粒子の添加率が高い場合には透過光量が低下し、好ましくない。また、1％未満では本発明の効果は充分に発揮されない。メタクリル樹脂を基体として用いる場合、メタクリル樹脂は通常屈折率が1.49程度であるため、架橋重合体微粒子の屈折率は1.50～1.54程度であることが望ましい。

【0013】
【発明の効果】本発明の光拡散性樹脂は、分散微粒子の粒径が小さく、かつ粒径分布がせまいため、高い光散乱性と高い光透過率を併せもち、照明カバー、各種ディスプレー、照明看板等に好適に利用できる。

【0014】
【実施例】以下、本発明を実施例により詳細に説明するが、本発明はこれらの実施例に限定されるものではない。なお、実施例中、部は重量部を、％は重量％を示す。

【0015】実施例1
ポリビニルアルコールの3％水溶液1000部に、メチルメタクリレート（MMA）79部、スチレン19部、エチレングリコールジメタクリレート2部及び2,2-アゾビスイソブチロニトリル1.0部の混合液を加えて微分散させ、撹拌しながら、窒素気流下で70℃にて15時間の重合を行なった。さらに分級操作を施し、平均粒径6.3μm、標準偏差が1.1μmである架橋重合体微粒子を得た。この微粒子の屈折率は、JIS K 7105に準拠して、顕微鏡によりベッケ線の移動を測定することにより求めた結果、1.514であった。上記で得た架橋重合体微粒子を用いて、厚さ1mmのアクリル樹脂板を作製した。すなわち、MMA91部、アクリル酸エチル9部、アゾビスイソブチロニトリル0.1部を混合し、60℃で1時間重合を行って、アクリ

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ル樹脂のシラップを得た。かかるシラップに上記微粒子を1.5部添加し分散させた。そしてこれを、ガスケットを装着した2枚のガラス板からなる型内に注入し、脱気後、80℃で2時間、さらに120℃で2時間加熱して重合を行なった。板厚を1mmに調整し、薄板状の光拡散性樹脂を得た。

【0016】実施例2～7
架橋重合体微粒子を合成する際の重合分散液の撹拌速度を変化させ得られる粒子径をコントロールした以外は、実施例1と同様な方法により粒径が異なる微粒子を得た。これを用いて、実施例1と同様にして表1に示す光拡散性樹脂を得た。

【0017】比較例1～3
重合後、精密分級を行なわなかった以外は実施例1と同様の方法にて微粒子の合成を行なった。この微粒子を用いて、実施例1と同様にして表1に示す光拡散性樹脂を得た。

【0018】試験例
上記の実施例及び比較例で得られた光拡散性樹脂の光透過性、光拡散能及び光拡散性を評価した。
〔方法〕
(1) 光透過性
光透過性は、積分球式光線透過率測定装置を用いて、全光線透過率を測定することにより評価した。
(2) 光拡散能
光拡散能は、平板状テストピースの後方より平行光線を入射し、前方に出てくる光の全光線透過率（T_t）と拡散透過率（T_d）の比、即ち、ヘーズ（haze）値を測定することにより評価を行なった。ヘーズ値（H）は数1により算出した。
【数1】

$$H (\%) = \frac{T_d（拡散透過率：\%）}{T_t（全光線透過率：\%）} \times 100$$

(3) 光拡散性
平板状テストピースの後方10cmに10Wの蛍光灯を配置し、前方より目視観察した。
○：蛍光灯の輪郭が見えない。
△：蛍光灯の輪郭がわずかに見える。
【表1】

5　　　　　　　　　　　　　　　　　　　　　6

実施例	平均粒径 （μm）	標準偏差 （μm）	使用量 （wt%）	全光線透過 率，%	ヘーズ 値，%	光分散性
1	6.3	1.1	1.5	85	94	○
2	10.5	1.995	2	85	93	○
3	10.5	1.995	4	83	94	○
4	10.5	1.995	8	75	94	○
5	2.2	0.088	1	87	95	○
6	4.1	0.39	2	87	94	○
7	15.7	2.041	1.5	85	92	○
比較例 1	10.5	2.8	2	71	96	○
2	6.3	1.696	1.5	62	95	△
3	4.1	1.388	2	79	95	○

〔結果〕その結果、表1に示すように、架橋重合体微粒
子の平均粒径及び粒径分布が一定範囲内にある本発明光
30

拡散性樹脂は、光透過性及び光拡散性ともに良好であっ
た。

PATENT ABSTRACTS OF JAPAN

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(54) LIGHT DIFFUSING RESIN

(57)Abstract:

PURPOSE: To obtain a composition suitable for lighting cover, having a fixed particle diameter distribution, small particle diameter, high light scattering properties and high light transmittance.

CONSTITUTION: Fine particles of crosslinked polymer having 1-30μm average particle diameter and a standard deviation of particle diameter distribution of ≤20% average diameter. The polymer has preferably 2-15μm average particle diameter, is spherical and is obtained by copolymerizing methyl methacrylate and/or styrene with a polyfunctional (meth)acrylate.

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http://www19.ipdl.jpo.go.jp/PA1/result/detail/main/...

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(54) [Title of the invention]
     Light diffusing resin

(57) [Abstract]

[Constitution] A light diffusing resin constituted by a substantially transparent resin having dispersed therein fine crosslinked polymer particles having an average particle size in the range of 1-30 μm, with the standard deviation of the particle size distribution being 20% or less of this average particle size.

[Constitution] Such light diffusing resins combine high light scattering and high light transmission and can be used advantageously for lighting covers, displays and illuminated signs and the like.

[Claims]

[Claim 1] Light diffusing resin constituted by a substantially transparent resin having dispersed therein fine crosslinked polymer particles having an average particle size in the range of 1-30 μm, with the standard deviation of the particle size distribution being 20% or less of this average particle size.

[Claim 2] Light dispersing resin described in Claim 1 wherein the substantially transparent resin is a resin in which the principal constituent is at least one selected from a methacrylic resin, polystyrene resin, polycarbonate resin, epoxy resin and poly(vinyl chloride resin).

[Claim 3] Light dispersing resin described in Claim 1 wherein the crosslinked polymer particles are of a copolymer of a methyl (meth)acrylate and/or styrene, with a polyfunctional (meth)acrylate.

[Detailed explanation of the invention]

[0001]

[Field of industrial application] The present invention relates to light diffusing resins ideal for use as materials in different types of displays, illuminated signs, translucent screens, lighting covers and the like for which a light diffusing function is required.

[0002]

[Prior art and problem which the invention is intended to solve] Materials comprising a transparent plastic with fine organic or inorganic particles dispersed therein are known as prior light diffusing materials used for lighting covers, screens and the like. Among the capabilities required in these materials, uniform diffusion of light over the widest possible range is important. In this connection, since the quantity of light emitted by a light source is constant, current practice is to optimise the material to give the most preferred illuminance and breadth, by altering parameters such as the concentration and particle size of the light diffusing material. Moreover,

various materials have been produced based on differences in refractive index between the resin and the fine particles constituting the light diffusing material as an index. However, no light diffusing materials exist which are fully satisfactory for applications such as screens for rear projection television or light diffusing electroluminescent (EL) substrate materials, which are required to have high light scattering.

[0003]

[Means for solving the problem] The present invention has been perfected as the result of concerted research by the inventor directed towards obtaining superior light diffusing materials in the light of the situation above, with the discovery that the particle size distribution of the fine particles dispersed within the resin is an important factor in determining light diffusion performance and that light diffusing resins which have outstanding light diffusion performance and do not colour the transmitted light can be obtained if the particle size distribution is within a set range.

[0004] Thus, the present invention offers light diffusing resins constituted by a substantially transparent resin having dispersed therein fine cross-linked polymer particles having an average particle size in the range of 1-30 μm, with the standard deviation of the particle size distribution being 20% or less of this average particle size.

[0005] The average particle size of the fine cross-linked polymer particles used in the present invention is in the range 1-30 μm, and is preferably in the range 2-15 μm. An average particle size of less than 1 μm is undesirable because the transmitted light is coloured; and more than 30 μm is less than ideal because the intensity of scattering of the transmitted light tends to be lowered.

[0006] In the present invention, the standard deviation of the particle size distribution is 20% or

less of the average particle size thereof: i.e. the fine particles need to have high monodispersity. When this standard deviation is greater than 20%, i.e. with polydisperse fine particles, it is impossible to achieve both satisfactory light scattering and satisfactory light transmission.

[0007] Although there is no specific restriction as to the shape of the fine crosslinked polymer particles, they are preferably spherical. In addition, the surface of the fine particles can be porous.

[0008] Fine crosslinked polymer particles having an average particle size and particle size distribution within these set ranges can be produced, for example, by grading fine crosslinked polymer particles obtained by using suspension polymerization, so as to regulate the particle size, or by using so-called seed polymerization in order to produce fine crosslinked polymer particles having a regulated particle size.

[0009] There is no specific restriction as to the polymer constituting the fine crosslinked polymer particles employed in the present invention, but examples include crosslinked styrene copolymers such as styrene/divinylbenzene, styrene/ethylene glycol dimethacrylate and styrene/butadiene copolymers, cross-linked (meth)acrylate ester copolymers such as methyl (meth)acrylate/divinylbenzene, methyl methacrylate/-ethylene glycol dimethacrylate and methyl (meth)acrylate/methylenebisacrylamide copolymers, cross-linked olefinic compolymers such as ethylene/butadiene, methyl vinyl ether/divinyloxybutane, vinyl acetate/-divinyloxybutane and vinyl chloride/divinylbenzene copolymers. When methacrylate resin is used as the base, fine particles obtained by copolymerizing methyl methacrylate and/or styrene with a polyfunctional (meth)acrylate can be ideally used. As such poly-functional (meth)acrylates, (poly)ethylene glycol di(meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate and tetraethylene glycol di(meth)acrylate, glycol

di(meth)acrylates such as propylene glycol di-(meth)acrylate, 1,3-butanediol di(meth)acrylate, tetra-ethylene glycol (meth)acrylate and neopentyl glycol (meth)acrylate and (meth)acrylates of polyhydric alcohols such as trimethylolpropane tri(meth)acrylate and pentaerythritol tetra(meth)acrylate can be employed.

[0010] The base resin of the light diffusing resin needs to be a substantially transparent resin, and the higher the transparency (light transmission) the better. Resins of this type such as methacrylic resins, epoxy resins, polycarbonate resins, polystyrene resins and poly(vinyl chloride) resins can be employed.

[0011] As the process for producing light diffusing resins of the present invention, for example, afore-mentioned fine crosslinked polymer particles can be dispersed in the polymerizable monomers or a syrup of partially polymerized polymerizable monomers and polymerized therewith, or the fine crosslinked polymer particles and a pre-prepared base polymer can be melt compounded and pressed. And when the light diffusing resin is to be formed into a thin film, a method such as screen-printing can be used.

[0012] The inclusion rate of fine crosslinked polymer particles in the light diffusing resin is preferably 1-10 wt%; a high percentage addition of fine particles is undesirable because light transmission is lowered. Similarly, with less than 1% it is impossible to obtain the full advantageous effects of the present invention. When a methacrylic resin is used as the base, it is desirable that the refractive index of the fine crosslinked polymer particles be of the order of 1.50-1.54, since the refractive index of methacrylic resins is ordinarily of the order of 1.49.

[0013]

[Effects of the invention] In light diffusing resins of the present invention the dispersed particles have a small particle size and a narrow particle size distribution, and as a consequence combine high light scattering and high light transmission and are ideal for

applications such as lighting covers, displays of different kinds and illuminated signs.

[0014]

[Examples] The present invention is described in more detail below by means of practical examples; however, the present invention is not restricted to these examples. In the examples, "parts" indicates parts by weight and "%" indicates wt%.

[0015] Example 1

A mixed solution of 79 parts of methyl methacrylate (MMA), 19 parts of styrene, 2 parts of ethylene glycol dimethacrylate and 1.0 part of 2,2-azobis-isobutyronitrile was added to 1000 parts of a 3% aqueous solution of poly(vinyl alcohol), finely dispersed therein and polymerized for 15 hours at 70°C under a stream of nitrogen gas, with continuous stirring. This was followed by a grading operation to obtain fine crosslinked polymer particles having an average particle size of 6.3 μm, with a standard deviation of 1.1 μm. The results of determination of the refractive index of these fine particles, found by determining shifts in the Bekke lines under a microscope in accordance with JIS K 7105, was 1.514. An acrylic resin sheet 1 mm thick was made using the fine crosslinked resin particles obtained above. Thus, 91 parts of MMA, 9 parts of ethyl acrylate and 0.1 part of azobisisobutyronitrile were mixed and polymerized for one hour at 60°C, to obtain an acrylic resin syrup. The aforementioned fine particles were added (1.5 parts) to this syrup and dispersed therein, and the mixture was injected into a mould comprising two sheets of glass fitted with a gasket, and after removing air it was polymerized by heating for 2 hours at 80°C and then for 2 hours at 120°C. This gave a light diffusing resin in the form of a thin sheet with the sheet thickness adjusted to 1 mm.

[0016] Examples 2-7

Fine particles with different particle sizes were obtained by the same method as in Example 1, except that the resulting particle size was controlled by altering

the speed of stirring of the liquid dispersion when synthesizing the fine crosslinked polymer particles. These were used as in Example 1 to obtain the light diffusing sheets indicated in Table 1.

[0017] Comparative examples 1-3

Particles were synthesized by the same method as in Example 1, without precise grading after polymerization. These fine particles were used as in Example 1 to obtain the light diffusing sheets indicated in Table 1.

[0018] Test examples

The light transmission, light scattering capability and light scattering of the light diffusing resins obtained in the aforementioned examples and comparative examples were evaluated.

[Methods]

(1) Light transmission

Light transmission was evaluated by measuring total light transmission using an integrating spherical light transmission meter.

(2) Light diffusing capacity

Light diffusing capacity was evaluated by illuminating a test piece in the form of a sheet from behind, and measuring the ratio of total light transmission (T_t) and diffuse light transmission (T_d) — i.e., the haze value (H). The haze value was calculated by means of Equation 1

[Equation 1]

$$H\ (\%) = [T_d\ (\text{diffuse light transmission: } \%)]/[T_t\ (\text{total transmission: } \%)] \times 100$$

(3) Light diffusion

A 10W fluorescent bulb was places at a distance of 10 cm behind the test piece in the form of a sheet and the test piece was observed visually from the front.

O : Outline of the fluorescent bulb not visible

Δ : Outline of the fluorescent bulb slightly visible

[Table 1]

Example	Average particle size (µm)	SD (µm)	Amount used (wt%)	Total light transmission %	Haze value %	Light diffusion
1	6.3	1.1	1.5	85	94	O
2	10.5	1.995	2	86	93	O
3	10.5	1.995	4	83	94	O
4	10.5	1.995	8	75	94	O
5	2.2	0.088	1	87	95	O
6	4.1	0.39	2	87	94	O
7	15.7	2.041	1.5	85	92	O
Comparison 1	10.5	2.8	2	71	96	O
2	6.3	1.696	1.5	62	95	Δ
3	4.1	1.368	2	73	95	O

[Results] As the results in Table 1 show, both light transmission and light diffusion were satisfactory for the light diffusing resins of the present invention, wherein the average particle size and particle size distribution of the fine crosslinked polymer particles were within set ranges.

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The Physics of
Glassy Polymers

Second edition

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J.G. (1990) *Polym. Eng.*

rial College of Science,
Department, Exhibition
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t, The Netherlands.]

Rubber toughening   8

C.B. Bucknall

8.1 INTRODUCTION

Glassy polymers are by definition hard and non-crystalline. Many glassy thermoplastics, and all thermosetting resins, also display another characteristic of glasses – brittleness. The discovery that materials as unpromising as polystyrene (PS) and epoxy resin can be toughened by the addition of 5–15% of a suitable rubber has therefore been of major importance to the plastics industry. Indeed, rubber toughening has proved so effective that the technology has been extended to almost all of the commercial glassy thermoplastics, including poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and even polycarbonate (PC), the toughest of the glassy polymers; it has also been applied to several thermosetting resins other than epoxies. In this chapter the prefix RT- will be used to denote rubber-toughened polymers, except for polystyrene (PS) and poly(styrene-co-acrylonitrile) (PSAN), where the acronyms HIPS (high impact polystyrene), and ABS (acrylonitrile–butadiene–styrene polymer) have become firmly established.

Toughness is the property of resisting fracture by absorbing and dissipating energy. Strength, on the other hand, is the ability to resist high stresses, and is obtained by suppressing deformation mechanisms, sometimes to the extent that the material becomes brittle under normal loading conditions. Conversely, toughness in rubber-modified polymers is achieved at some sacrifice of strength and stiffness. Whereas glassy polymers have shear moduli of about 1000 MPa and Young's moduli in the range 2500–3500 MPa, rubbers have very low shear moduli, typically between 0.1 and 1.0 MPa. The reductions in modulus brought about by adding rubber are acceptable if they are accompanied by a substantial increase in toughness.

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発明の数　1
審査請求　未請求

（全 6 頁）

㊸光拡散性アクリル樹脂成形体

㉑特　　　願　昭57—148877
㉒出　　　願　昭57(1982) 8 月27日
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明　　　細　　　書

1　発明の名称
　　光拡散性アクリル樹脂成形体
2　特許請求の範囲
　メチルメタクリレート系重合体100重量部
に対し下記の架橋ポリマーを1〜30重量部配
合した樹脂組成物を成形して得られる光拡散性
アクリル樹脂成形体。
架橋ポリマー：
　アルキル基の炭素数が1〜8の
　　　　　　アルキルメタクリレート　50〜10重量%
　アルキル基の炭素数が1〜8の
　　　　　　アルキルアクリレート　　10〜40重量%
　芳香族ビニルモノマー　　　　　　0〜20重量%
　その他のモノエチレン性不飽和
　　　　　　　　　　モノマー　　0〜20重量%
からなる非架橋性モノマー100重量部と架
橋性モノマー0.5〜3重量部を屈間混合して
得られる粒子径10〜500μ、ゲル含有量
50〜90重量%、膨潤度3〜25なる架橋

ポリマー。
3　発明の詳細な説明
　本発明は高い光拡散性を有すると同時に高い
光線透過率をも兼ね備えた照明カバー等に適し
た光拡散性アクリル樹脂成形体に関する。
　従来アクリル樹脂成形体に光拡散効果を与え
る方法としては基材樹脂に硫酸バリウム、酸化
チタン、タルク等の無機化合物の微粒子を分散
させるか、あるいは型模様のあるダイスで押出
すか、エンボスロールを通すなどの機械的手段
で凹凸模様を付与する方法が一般的であった。
　しかしながら型模様のあるダイスやエンボス
ロールを用いる方法ではある程度光拡散効果の
ある成形板は得られても、照明カバー等の用途
に応じた各種形状に二次加工した場合、表面の
凹凸が失なわれて十分な光拡散効果を示す、成
形体が得られないという重大な欠点があった。
　また、無機化合物の微粒子を基材樹脂に添加
した場合には一般に十分な光拡散性は得られて
も光線透過率の低下が大きいという欠点があり、

しかも衝撃強度等の素材固有の物性を低下させるという欠点をも有していた。

本発明はこれら従来方法の欠点を改善したものであり、特定の架橋ポリマーをメチルメタクリレート系重合体に特定量配合することにより高い光拡散性と高い光線透過率とを兼ね備え、かつ二次加工をしても光拡散性が低下しない光拡散性アクリル樹脂成形体とし得ることを見出し本発明に到達した。

本発明はメチルメタクリレート系重合体100重量部に対し下記の架橋ポリマーを1～30重量部配合した樹脂組成物を成形して得られる光拡散性アクリル樹脂成形体である。

架橋ポリマー：
アルキル基の炭素数が1～4の
アルキルメタクリレート 50～90重量%
アルキル基の炭素数が1～8の
アルキルアクリレート 10～40重量%
芳香族ビニルモノマー 0～20重量%
その他のモノエチレン性不飽和
モノマー 0～20重量%

系重合体に添加して成形してもその成形体表面は粗い感じであり、照明カバー等の素材としては好ましくないものとなる。一方粒子径が10μ未満の架橋ポリマー、特に乳化重合により得られる1μ以下の粒子径のものでは十分な光拡散効果は得られない。

本発明で用いられる架橋ポリマーを構成するモノマー類にもその適正な組成域が存在し、それ以外の組成では光拡散効果が不十分だったり、光線透過率が不十分だったり、あるいはこれを配合、成形して得られる成形体表面が粗い感じのものしか得られない。

本発明で用いられる架橋ポリマーを構成するのに適したモノマー組成はアルキル基の炭素数が1～4のアルキルメタクリレート50～90重量%、アルキル基の炭素数が1～8のアルキルアクリレート10～40重量%、芳香族ビニルモノマー0～20重量%およびその他のモノエチレン性不飽和モノマー0～20重量%からなる非架橋性モノマーとこれら非架橋性モノマ

からなる非架橋性モノマー100重量部と架橋性モノマー0.5～5重量部を懸濁混合して得られる粒子径10～500μ、ゲル含有量50～90重量%、膨潤度3～25なる架橋ポリマー。

本発明はメチルメタクリレート系重合体の光拡散剤として特定の組成、粒子径、ゲル含有量、膨潤度を有する架橋ポリマーを配合したことを特徴とするものであり、これにより従来の無機系の光拡散剤を配合した場合では決して得られなかった優れた性能を有する光拡散性アクリル樹脂成形体を提供するものである。

本発明の特徴の1つは光拡散剤として用いられる架橋ポリマーの製造方法およびその生成粒子径の規制である。即ち架橋ポリマーは懸濁重合により得られる粒子径10～500μ、好ましくは35～300μのものが用いられる。粒子径が500μを超える架橋ポリマーではたとえその組成やゲル含有量、膨潤度が本発明で規制する範囲内であってもメチルメタクリレート

一の合計量100重量部あたり0.5～5重量部の架橋性モノマーから成る組成である。

アルキル基の炭素数が1～4のアルキルメタクリレートとしてはメチルメタクリレート、エチルメタクリレート、プロピルメタクリレート、ブチルメタクリレート等を単独で又は混合して用いることが出来るがメチルメタクリレートが特に好ましい。アルキルメタクリレートの使用量は50～90重量%、好ましくは55～70重量%である。

アルキル基の炭素数が1～8のアルキルアクリレートとしてはメチルアクリレート、エチルアクリレート、プロピルアクリレート、ブチルアクリレート、2-エチルーヘキシルアクリレート等を単独で又は混合して用いることが出来るがブチルアクリレート、2-エチルーヘキシルアクリレート等ガラス転移温度が低いものがより好ましい。アルキルアクリレートの使用量は10～40重量%、好ましくは25～40重量%である。

芳香族ビニルモノマーとしてはスチレン、α
ーメチルスチレン、ビニルトルエン、ハロゲン
化スチレン等を用いることが可能であり、その
使用量は0～20重量%、好ましくは2～15
重量%である。芳香族ビニルモノマーを20重
量%を超えて用いると光線透過率等の低下をま
ねくので好ましくない。架橋ポリマーの屈折率
調整、架橋度のコントロールなどの点からは
20重量%を超えない範囲で用いた方が良い結
果が得られる場合が多い。

その他のモノエチレン性不飽和モノマーは特
に用いる必要はないが、20重量%を超えない
範囲で用いることは可能である。具体例として
はフマール酸、マレイン酸および共重合可能な
カルボン酸とそのエステル類、アクリル酸、メ
タアクリル酸、アクリロニトリル、ハロゲン化
ビニル、およびビニルエステル類等が使用可能
である。

架橋性モノマーとしては、分子内に2個以上
の不飽和結合を持つ化合物が用いられるが、特
にその2個以上の不飽和結合のうちの少なくと
も1個がアリル基である様な化合物であること
が好ましい。このようなアリル基含有架橋モノ
マーを用いることにより、本発明の特徴の1つ
である架橋ポリマーの膨潤度、ゲル含量のコン
トロールが容易になるばかりでなく、架橋ポリ
マー内部に適度の架橋分布を与えるので良好な
特性が得られやすくなる。アリル基を含有する
架橋性モノマーとしてはアリルメタクリレート、
トリアリルシアヌレート、トリアリルイソシア
ヌレートが代表的なものであり、アリルメタクリ
レートが特に好ましい。さらにこれら以外のそ
の他の架橋性モノマーとしてはエチレングリコ
ールジメタクリレート等のアルキレングリコー
ルの不飽和カルボン酸エステル；プロピレング
リコールジアリルエーテル等のアルキレングリ
コールの不飽和アルコールエーテル；ジビニル
ベンゼン等の多価ビニルベンゼン等があげられ
る。架橋性モノマーの添加量は、前記非架橋性
モノマーの合計量100重量部あたり0.5～5

重量部であり、特に1.0～4重量部であること
が好ましい。

本発明のもう1つの特徴はある特定のゲル含
有量および膨潤度を有する架橋ポリマーを拡散
剤として用いるという事である。

下記に示す測定法で得られたゲル含有量の値
が50～90重量%、好ましくは60～85重
量%でかつ膨潤度が2～25、好ましくは7～
20の架橋ポリマーを用いた場合にのみメチル
メタクリレート系重合体に対する優れた光拡散
効果を与える。

ゲル含有量が50重量%未満の架橋ポリマー
あるいは膨潤度が25を超える架橋ポリマーを
用いた場合には十分な光拡散効果が得られない
ばかりか全体的にいくぶんヘイズイになり光線
透過率も低下するので好ましくない。逆にゲル
含有量が90重量%を超えるか、あるいは膨潤
度が7未満の架橋ポリマーを用いた場合には成
形体表面は荒れた感じになり、特殊な場合を除
き照明カバー等の用途には向かないものになる。

（ゲル含有量・膨潤度の測定法）

所定量の架橋ポリマーを秤量ビンに秤量し、
約100倍量のメチルエチルケトン(MEK)
中に48時間浸漬する。浸漬後余分のMEK
をデカンテーションにより十分に除去し、
MEKで膨潤状態にある試料の重量を求める。
次いで減圧乾燥によりMEKを乾燥除去し試
料の絶乾重量を測定する。算出は次式に従う。

$$\text{ゲル含有量（重量\%）} = \frac{\text{絶乾重量（MEK浸漬後）}}{\text{採取試料重量}} \times 100$$

$$\text{膨潤度} = \frac{\text{MEK膨潤状態の試料重量} - \text{絶乾重量}}{\text{絶乾重量}}$$

架橋ポリマーのゲル含有量、膨潤度の調整は
主に用いる架橋性モノマーの種類、量の調整お
よび適切の連鎖移動剤の使用により行なわれる。
連鎖移動剤としては炭素数2～20のアルキル
メルカプタン、エステル系メルカプタン等通常
用いられるものを用いることが出来る。

架橋ポリマーの懸濁重合は通常行なわれる方
法で行なう事が出来、用いる開始剤、懸濁安定

剤については特に制限はないが、粒子径、ゲル
含有等の物性が好ましい範囲から逸脱しない様
その使用量等について注意が必要である。

　本発明におけるメチルメタクリレート系重合
体とはメチルメタクリレートの単独重合体もし
くはメチルメタクリレートと他のコモノマー、
例えばメチルアクリレート、エチルアクリレー
ト、n-ブチルアクリレート、エチルメタクリ
レート等との共重合体でメチルメタクリレート
成分が55%以上のものを言う。

　本発明における架橋ポリマー系拡散剤の使用
量はメチルメタクリレート系重合体100重量
部に対し、1～20重量部、好ましくは5～15
重量部である。

　メチルメタクリレート系重合体と架橋ポリマ
ー系光拡散剤との混合はヘンシェルミキサーを
用いる等通常の方法で行なうことが出来る。

　メチルメタクリレート系重合体と架橋ポリマ
ー系拡散剤との混合物は通常のメチルメタクリ
レート系重合体と同様の方法、すなわち押出し

在、射出成形圧等の方法により成形体とするこ
とが出来る。

　なお本発明の目的を達成する範囲内で、商品
価値を高める為、微量の染顔料、ブルーイング
剤、蛍光増白剤、光安定剤、熱安定剤その他の
添加剤を別に配合添加することは差しつかえな
い。

　この様にして得られた成形体は優れた光拡散
効果と高い光線透過率とを兼ね備えており、照
明カバー等の素材として好適なものである。

　以下実施例により更に詳細に説明するが本発
明はこれら実施例に限定されるものではない。

実施例1
(1)　架橋ポリマーの製造
　攪拌器、還流冷却器、チッ素ガス導入口等
のついた反応容器に次の化合物を仕込んだ。

　メチルメタクリレート　　　　　60重量部
　n-ブチルアクリレート　　　　　30重量部
　スチレン　　　　　　　　　　　10重量部

　アリルメタクリレート　　　　15重量部
　t-ドデシルメルカプタン　　　0.3重量部
　アゾビスイソブチロニトリル　0.5重量部
　ポリビニルアルコール　　　　1.0重量部
　水　　　　　　　　　　　　　200重量部

　容器内を十分にチッ素ガスで置換した後、
上記化合物の混合物を攪拌しながら70℃ま
で加熱し、チッ素ガス中で重合を進めた。　時
間後に90℃まで昇温し、90℃に1時間
保持して重合を完了させた。重合終了後脱水・
水洗・乾燥して粒状ビーズを得た。

　得られたビーズの平均粒子径は120μで
あり、ゲル含有量は75重量%、膨潤度は
11であった。

(2)　アクリル樹脂成形体の製造
　メチルメタクリレート系重合体（三菱レイ
ヨン（株）製、アクリペットMDK）100重
量部に対し、(1)で得られた架橋ポリマー10
重量部を配合し、ヘンシェルミキサーを用い
てよく混合した後、押出機を用いてペレット

化した。

　得られたペレットを80℃で一昼夜乾燥し
た後、同じ押出機を用い230℃で押出して
2.5㎜厚の押出板を成形した。

　得られた成形板の全光線透過率、曇価を積
分球式ヘーズメーターで測定した。またその
60度鏡面光沢度をデジタル変角光沢計（ス
ガ試験機製）で測定するとともに、成形板の
表面の状態を目視にて判定した。

　この成形板の全光線透過率は55%、曇価
は79であり、60度鏡面光沢度は33であ
った。また表面状態は均一で粗い感じはなく
優れたものであった。

参考例1
　ポリビニルアルコールの量を0.3重量部にす
る他は実施例1-(1)と同様にして架橋ポリマー
を得た。得られた架橋ポリマーのゲル含有量お
よび膨潤度は実施例1-(1)とはほぼ同じであった
が、その平均粒子径は約100μとかなり大を

かつた。

この架橋ポリマーを節別し、その32メッシュ（500μ）通過分を実施例ノー(l)で得た架橋ポリマーのかわりに用いる他は、実施例ノー(l)と同様の手順で押出板を製造し、同様に評価した。

この成形板の全光線透過率は92、5、評価は76であつたが表面は非常にザラザラした荒れた感じであり、照明カバー等には好ましくないものであつた。

参考例2

実施例ノー(l)で用いたのと同様の反応容器に次の化合物を仕込んだ

メチルメタクリレート	60 重量部
n-ブチルアクリレート	30 重量部
スチレン	10 重量部
アリルメタクリレート	2.5 重量部
t-ドデシルメルカプタン	0.3 重量部
過硫酸カリウム	0.3 重量部

スルフオコハク酸のエステルソーダ塩　　2.5 重量部

水　　　　　　　　　　　　　　250 重量部

容器内を十分にチッ素ガスで置換した後、上記化合物の混合物を撹拌しながら70℃まで昇温し、そのまま5時間保持して重合を完了させた。得られたラテックス中のポリマー粒子は約0.2μの粒子径を有していた（光透過法で測定）。このラテックスに5重量部の塩化カルシウムを添加して塩折し、さらに脱水・水洗・乾燥して粉末状の架橋ポリマーを得た。

この乳化重合により得られた架橋ポリマーを実施例ノー(l)で得た架橋ポリマーのかわりに用いる他は全く実施例ノー(l)と同様にして押出板を製造し同様に評価した。

この成形板は全光線透過率8.9 %、評価10、60度鏡面光沢度109であり、光拡散効果が不十分で照明カバーとして不向きなものであつた。

実施例2

実施例ノー(l)で用いたのと同じ反応容器に次の化合物を仕込み実施例ノー(l)と同様の手順で粒状の架橋ポリマーを得た。

メチルメタクリレート	35 重量部
ブチルメタクリレート	30 重量部
n-ブチルアクリレート	30 重量部
スチレン	5 重量部
アリルメタクリレート	2.5 重量部
n-オクチルメルカプタン	0.3 重量部
ラウロイルパーオキサイド	2.5 重量部
第三リン酸カルシウム	10 重量部
界面活性剤	0.01 重量部
水	200 重量部

得られたビーズ状架橋ポリマーの平均粒子径は約10μであり、ゲル含有量は77重量%、膨潤度は15であつた。

このビーズ状架橋ポリマーを実施例ノー(l)で製造した架橋ポリマーのかわりに用いる他は、実施例ノー(l)と同様の手順で押出板を製造し、

同様の手順で評価した。

この押出板の全光線透過率は65 %、評価は77、60度鏡面光沢度は27であり、表面状態も均一で極めて良好であつた。

参考例3

実施例ノー(l)で用いたのと同じ反応容器にアリルメタクリレートを除く実施例2で用いた化合物を仕込み、実施例ノー(l)と同様の手順で粒状の未架橋ポリマーを得た。

得られたビーズ状ポリマーの平均粒子径は約10μであり、ゲル含有量は0であつた。

この未架橋ポリマーを実施例ノー(l)で製造した架橋ポリマーのかわりに用いる他は実施例ノー(l)と同様の手順で押出板を製造し、同様の手順で評価した。

この成形板はやや曇つた感じではあるが光拡散度は低く、また60度鏡面光沢度が115と高く、照明用カバー等の用途には不向きなものであつた。

参考例 *

　実施例ノ－(1)で用いたのと同じ反応容器に、
アリルメタクリレートを7重量部用いる他は実
施例2と同じ化合物を仕込み、実施例ノ－(1)と
同様の手順で粒状の架橋ポリマーを得た。

　得られた架橋ポリマーの平均粒子径は約90
μであり、ゲル含有量は76重量％、膨潤度は
2.5であった。

　この架橋ポリマーを実施例ノ－(1)で得た架橋
ポリマーのかわりに用いる他は実施例ノ－(4)と
同様にして押出板を製造し、同様に評価した。

　この成形板は表面が完くザラザラしており、
照明カバー等の用途には不向きなものであった。

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—308—

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(54) LIGHT-DIFFUSING ACRYLIC RESIN MOLDING

(57)Abstract:

PURPOSE: To provide a light-diffusing acrylic resin molding which has both high light diffusing ability and high light transmittance and does not cause lowering in the light diffusing ability even when fabricated, by blending a specified quantity of a specified crosslinked polymer with a methyl methacrylate polymer.

CONSTITUTION: A resin compsn. obtd. by blending 1W30pts.wt. crosslinked polymer with 100pts.wt. methyl methacrylate polymer is molded to obtain the titled molding. Said crosslinked polymer has a particle size of 10W500μ, a gel content of 50W90wt% and a degree of swelling of 3W25 and can be obtd. by suspension- polymerizing 0.5W5pts.wt. crosslinkable monomer and 100pts.wt. non-crosslinkable monomer mixture consisting of 50W90wt% C1WC4 alkyl methacrylate, 10W40wt% C1WC8 alkyl acrylate, 0W20wt% arom. vinyl monomer and 0W 20wt% monoethylenically unsaturated monomer.

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(54) Light-diffusing acrylic resin molding

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SPECIFICATION

1. TITLE OF THE INVENTION

5   Light-diffusing acrylic resin molding

2. WHAT IS CLAIMED IS :

        Light-diffusing acrylic resin molding which is
10 produced by molding a resin composition in which 1 - 30
parts by weight of the crosslinked polymer noted below
is blended with 100 parts by weight of a methyl
methacrylate polymer.
Crosslinked polymer :
15   Crosslinked polymer with a particle diameter of 10
- 500 μ, a gel content of 50 - 90% by weight and a
swelling degree of 3 - 25 which is produced by
suspension polymerization of 0.5 - 5 parts by weight of
a crosslinkable monomer and 100 parts by weight of a
20 non-crosslinkable monomer consisting of
        alkyl methacrylate in which the number of carbon
atoms of the alkyl groups is 1 - 4
50 - 90% by weight
        alkyl acrylate in which the number of carbon atoms
25 of the alkyl groups is 1 - 8
10 - 40% by weight
        aromatic vinyl monomer   0 - 20% by
weight
        other monoethylenic unsaturated monomer 0 - 20% by
30 weight

3. DETAILED DESCRIPTION OF THE INVENTION

        The present invention relates to a light-diffusing
35 acrylic resin molding which possesses an excellent
light diffusion property and, at the same time, also
has high light transmittance and which is suitable as a
lighting cover, etc.

Conventionally, the usual method of imparting a light diffusion effect to acrylic resin moldings is to disperse fine particles of an inorganic compound such as barium sulfate, titanium oxide or talc, etc. in a base resin or to impart an irregular pattern by mechanical means such as effecting extrusion with a die which has a pattern of effecting passage through embossing rolls.

However, with a method using a die which has a pattern or embossing rolls, even if a molding which has a light diffusion effect to a certain degree is produced, there is the major drawback that when secondary processing to various shapes suitable for lighting covers, etc. is effected, the surface irregularities are lost, and so there is failure to produce a molding which displays a satisfactory light diffusion effect.

Also, in cases in which fine particles of an inorganic resin are added to a base resin, although a satisfactory light diffusion effect is generally achieved, there is the drawback that there is a considerable fall in the light transmittance, and there is drawback that the base resin's physical properties such as its impact strength, etc. deteriorate.

The present invention is one which makes improvement in respect of these drawbacks of conventional methods, and it has been achieved as the result of the discovery that a light-diffusing acrylic resin molding which combines an excellent light diffusion property and high light transmittance and whose light diffusion property does not deteriorate even if secondary processing is effected can be produced by making a specific admixture of a specific crosslinked polymer in a methyl methacrylate polymer.

The invention is a light-diffusing acrylic resin molding which is produced by molding a resin composition in which 1 - 30 parts by weight of the crosslinked polymer noted below is blended with 100 parts by weight of a methyl methacrylate polymer. Crosslinked polymer :

Crosslinked polymer with a particle diameter of 10 - 500 μ, a gel content of 50 - 90% by weight and a swelling degree of 3 - 25 which is produced by suspension polymerization of 0.5 - 5 pts.wt. of a crosslinkable monomer and 100 pts.wt. of a non-crosslinkable monomer consisting of

alkyl methacrylate in which the number of carbon atoms of the alkyl groups is 1 - 4 50 - 90% by weight	
alkyl acrylate in which the number of carbon atoms of the alkyl groups is 1 - 8, 10 - 40 wt%	
aromatic vinyl monomer	0 - 20 wt%
other monoethylenic unsaturated monomer	0 - 20 wt%

The invention is characterized by the fact that a crosslinked polymer with a specific composition, particle diameter, gel content and swelling degree is admixed as the light diffusion agent of a methyl methacrylate polymer. As a result of this, the invention provides a light-diffusing acrylic resin molding possessing an excellent performance which has never been achieved in cases in which conventional inorganic light diffusion agents are admixed.

One special feature of the invention is constituted by the method of manufacture of the crosslinked polymer which is used as a light diffusion agent and the prescription of the particle diameter that is produced. More specifically. The crosslinked polymer which is used is one whose particle diameter which has been produced by suspension polymerization is 10-500 μ, preferably 35-200 μ. With a crosslinked

polymer whose particle diameter exceeds 500 μ, even if its composition, gel content and swelling degree are within the ranges which are prescribed in the invention, and molding is effected after it is added to a methyl methacrylate polymer, the surface of the resulting molding feels rough, and the molding is undesirable as material for a lighting cover, etc . On the other hand a satisfactory light diffusion effect is not achieved by a crosslinked polymer whose particle diameter is less than 10 μ, especially one with a particle diameter of 1 μ or less which is produced by emulsification polymerization.

Appropriate composition regions also exist for the monomers which constitute the crosslinked polymer which is used in the invention and, with compositions outside these regions, the light diffusion effect is unsatisfactory, or the light transmittance is unsatisfactory, or the only moldings produced by blending these compositions and effecting molding are ones whose surface feels rough.

A monomer composition which is suitable for constituting the crosslinked polymer which is used in the invention is a composition consisting of 50-90 wt% of an alkyl methacrylate in which the number of carbon atoms of the alkyl groups is 1-4, 10-40 wt% of an alkyl acrylate in which the number of carbon atoms of the alkyl groups is 1-8, 0-20 wt% of an aromatic vinyl monomer, 0-20 wt% of another monoethylenic unsaturated monomer, and 0.5 - 5 pts.wt. of a crosslinkable monomer per 100 pts.wt. of the combined total of non-crosslinkable monomers.

Methyl methacrylate, ethyl methacrylate, propyl methacrylate and butyl methacrylate, etc. can be used alone or mixed as the alkyl methacrylate in which the number of carbon atoms of the alkyl groups is 1-4, and methyl methacrylate is particularly preferable. The

amount of the alkyl methacrylate used is 50-90 wt%, preferably 55-90 wt%.

Methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, or 2-ethyl-hexyl acrylate, etc. can be used alone or mixed as the alkyl acrylate in which the number of carbon atoms of the alkyl groups is 1-8, and substances such as butyl acrylate and 2-ethyl-hexyl acrylate, etc. whose glass transition temperature is low are the more preferable. The amount of the alkyl acrylate used is 10-40 wt%, preferably 25-40 wt%.

It is possible to use styrene, α-methylstyrene, vinylstyrene or halogenated styrene, etc. as the aromatic vinyl monomer, and the amount thereof used is 0-20 wt%, preferably 3-15 wt%. The use of more than 20 wt% of an aromatic vinyl monomer is undesirable, since it causes deterioration of the light transmittance, etc. From the point of view of adjustment of the refractive index and control of the degree of crosslinking, etc. of the crosslinked polymer, it is found in most cases that it is better to use an amount not exceeding 20 wt%.

It is not particularly necessary to use another monoethylenic unsaturated monomer, but it is possible to use one in an amount not exceeding 20 wt%. By way of specific examples, it is possible to use fumaric acid, maleic acid, copolymerizable carboxylic acid and esters thereof, acrylic acid, methacrylic acid, acrylonitrile, halogenated vinyl and vinyl esters, etc.

A compound which has 2 or more unsaturated bonds in its molecules can be used as the crosslinkable monomer, and it is particularly preferable that it be a compound in which at least 1 within the 2 or more unsaturated bonds is an allyl group. The use of such a crosslinkable monomer which contains allyl groups makes it easy to achieve good characteristics, since, as well

as making the control of the swelling degree and the gel content of the crosslinked polymer easy, it gives a suitable crosslinking distribution in the crosslinked polymer.   By way of crosslinkable monomers, which contain allyl groups, there are, as typical substances, allyl methacrylate, triallyl cyanurate and triallyl isocyanate, allyl methacrylate being particularly preferable.   By way of other crosslinkable monomers apart from these, it is possible to cite alkylene glycol unsaturated carboxylic acid esters such as ethylene glycol dimethacrylate, etc.; alkylene glycol unsaturated alcohol ethers such as propylene glycol diallyl ether, etc.; and polyvalent vinyl benzenes such as divinyl benzene, etc. The amount of crosslinkable monomer added is 0.5 - 5 pts.wt. per 100 pts.wt. of the combined total of the non-crosslinkable monomers noted above, 1.0 - 4 pts.wt. being particularly preferable.

Another special feature of the invention is that a crosslinked polymer which has a specific gel content and swelling degree is used as a diffusion agent.

An excellent light diffusion effect is imparted to the methyl methacrylate polymer only when a crosslinked polymer whose gel content found by the measurement method described below is 50-90 wt%, preferably 60-85 wt%, and whose degree of swelling is 3-25, preferably 7-20.

If a crosslinked polymer whose gel content is less than 50 wt% or a crosslinked polymer whose degree of swelling exceeds 25 is used, this is undesirable, since a satisfactory light diffusion effect fails to be achieved and, in addition, the material becomes rather hazy overall and the light transmittance deteriorates. Conversely, if a crosslinked polymer whose gel content exceeds 90% or whose degree of swelling is less than 3 is used, the molding has a surface which feels rough

and, except in special cases, it is not suited to applications such as that of a lighting cover, etc.

Methods of measurement of gel content and degree of swelling:

A set amount of crosslinked polymer is weighed in a weighing bottle and is immersed for 48 hours in an amount of methyl ethyl ketone (MEK) that is about 100 times greater. After the immersion, thorough removal of excess MEK is effected by decantation, the weight of the sample which has been brought to a swollen state by the MEK is determined, and then the MEK is dried and removed by vacuum drying and the absolute dry weight of the sample is measured. Calculations by the following formulas are made.

Gel content (wt%) =

$$\frac{\text{Absolute dry weight (after MEK immersion)}}{\text{Weight of sample that is taken}} \times 100$$

Degree of swelling

$$\frac{\text{Weight of sample in MEK swelling state} - \text{absolute dry weight}}{\text{Absolute dry weight}}$$

Adjustment of the gel content and the degree of swelling of the crosslinked polymer is mainly effected through the adjustment of the type and the amount of the crosslinkable monomer that is used and the use of a suitable amount of a chain shift agent. Normally employed substances such as a 2-20C alkyl mercaptan or an ester-based mercaptan can be used as a chain shift agent.

Suspension polymerization of the crosslinked polymer can be effected by normally employed procedure and, although there are no particular restrictions regarding the initiator and suspension stabilizer which are used, it is necessary to take care over the used amounts, etc., in order to avoid departure from the

preferred ranges for characteristics such as the
particle diameter and the gel content, etc.

What is meant by a methyl methacrylate polymer in
the invention, is a methyl methacrylate homopolymer or
a copolymer of methyl methacrylate and another monomer,
eg, methyl acrylate, ethyl acrylate, n-butyl acrylate
or ethyl methacrylate, etc. in which the methyl
methacrylate component is 85% or more.

The amount of crosslinked polymer system diffusion
agent used in the invention is 1-30 pts.wt., preferably
5-15 pts.wt. relative to 100 pts.wt. of the methyl
methacrylate polymer.

The methyl methacrylate polymer and the
crosslinked polymer system light diffusion agent can be
mixed by normally employed procedure such as the use of
a Henschel mixer, etc.

The mixture of the methyl methacrylate polymer
and the crosslinked polymer system light diffusion
agent can be made a molding by the same procedure as
that for ordinary methyl methacrylate polymers, i.e.
extrusion or injection molding procedure.

There is no objection if, within the range in
which the object of the invention is achieved, small
amounts of a dye pigment, a bluing agent, a fluorescent
whitener, a heat stabilizer or other additives are
added for the purpose of increasing the product value.

The molding which is produced in this manner
combines an excellent light diffusion effect and high
light transmittance, and is very suitable as material
for lighting covers, etc.

Below, a description in further detail is given by
means of examples of implementation, though the

invention is not limited to these examples of implementation.

Example 1

(1) Manufacture of crosslinked polymer

The following compounds were charged into a reaction vessel provided with a stirrer, a reflux cooler and a nitrogen gas introduction port, etc.

Methyl methacrylate	60 pts.wt.
n-butyl acrylate	30 pts.wt.
styrene	10 pts.wt.
allyl methacrylate	1.5 pts.wt.
t-dodecyl methacrylate	0.3 pts.wt.
azobisisobutyronitrile	0.5 pts.wt.
polyvinyl alcohol	1.0 pt.wt.
water	200 pts.wt.

After the interior of the vessel had been thoroughly replaced by nitrogen gas, the mixture of the compounds noted above was heated to 70°C while being stirred, and polymerization was caused to proceed in the nitrogen gas. After 4 hours, the temperature was raised to 90°C, and polymerization was completed by holding at 90°C for 1 hour. After the completion of polymerization, dewatering, water-washing and drying were effected, and granular beads were obtained.

The average particle diameter of the beads that were obtained was 120 μ, the gel content was 75 wt% and the swelling degree was 11.

(2) Manufacture of acrylic resin molding

10 pts.wt. of the crosslinked polymer obtained in (1) was added to 100 pts.wt. wt. of a methyl methacrylate polymer (Acrylpet MDK manufactured by

Mitsubishi Rayon KK) and thoroughly mixed therewith by means of a Henschel mixer, and then pellets were produced by means of an extrusion machine.

5   The pellets that were produced were dried for 24 hours at 80°C, and then a 2.5 mm thick sheet was molded by extruding the pellets 220°C by means of the same extrusion machine.

10   The total light transmittance and the haze value of the molded sheet that was produced were measured by an integrating bulb type haze meter, its 60-degree specular gloss was measured by a digital variable-angle gloss meter (manufactured by Suga Shikenki), and the
15 state of the molding's surface was judged visually.

The total light transmittance of this molding was 85%, its haze value was 79 and its 60 degree specular gloss was 23. Also, it was an excellent product whose
20 surface was uniform and without any impression of roughness.

Reference Example 1

25   A crosslinked polymer was produced in the same way as in Example 1 (1) except that the amount of polyvinyl alcohol was made 0.3 pts.wt. The gel content and the swelling degree of the crosslinked polymer that was produced were about the same as in Example 1 (1), but,
30 at 600 μ, its average particle diameter was considerably greater.

This crosslinked polymer was screened, an extruded sheet was manufactured by the same procedure as in
35 Example 1 (2) except that the 32 mesh (500 μ) pass fraction of this polymer was used instead of the crosslinked polymer that was produced in Example 1 (1), and evaluations were made in the same way.

The total light transmittance of this molding was 92% an its haze value was 76, but its surface had an extremely gritty rough feel, and it was undesirable as a molding for lighting covers, etc.

5

Reference Example 2

The following compounds were charged into a reaction vessel like that used in Example 1 (1).

10

Methyl methacrylate	60 pts.wt.
n-butyl acrylate	30 pts.wt.
styrene	10 pts.wt.
allyl methacrylate	1.5 pts.wt.
t-dodecyl mercaptan	0.3 pts.wt.
potassium persulfate	0.3 pts.wt.
sulfosuccinic acid ester sodium salt	1.5 pts.wt.
water	250 pts.wt.

20

After the interior of the vessel had been thoroughly replaced by nitrogen gas, the mixture of the compounds noted above was heated to 70°C while being stirred, and was held as it was for 5 hours to complete polymerization. The polymer particles in the latex that was produced had a particle diameter of approximately 0.2 µ (measurement by light transmission method). Salting out was effected by adding 5 pts.wt. of calcium chloride to this latex, and a crosslinked polymer in powder form was obtained by further effecting dewatering, water-washing and drying.

An extruded sheet was manufactured by exactly the same procedure as in Example 1 (2) except that this crosslinked polymer which had been produced by emulsification polymerization was used instead of the crosslinked polymer that was produced in Example 1 (1), and evaluations were made in the same way.

The total light transmittance of this molded sheet was 89%, its haze value was 1.0, its specular gloss was 107, and as its light diffusion effect was unsatisfactory, it was not suitable as a lighting cover.

Example 2

The following compounds were charged into a reaction vessel which was the same as that used in Example 1 (1), and a crosslinked polymer was produced by the same procedure as in Example 1 (1).

Methyl methacrylate	35 pts.wt.
butyl methacrylate	30 pts.wt.
n-butyl acrylate	30 pts.wt.
styrene	5 pts.wt.
allyl methacrylate	1.5 pts.wt.
n-octyl mercaptan	0.3 pts.wt.
lauroyl peroxide	1.5 pts.wt.
tribasic calcium phosphate	1.0 pt.wt.
surfactant	0.01 pts.wt.
water	200 pts.wt.

The average particle diameter of the crosslinked polymer that was obtained in the form of beads was approximately 90 μ, it's gel content was 77 wt%, and its swelling degree was 13.

An extruded sheet was manufactured by the same procedure as in Example 1 (2) except that this crosslinked polymer in the form of beads was used instead of the crosslinked polymer that was manufactured in Example 1 (1), and evaluations were made in the same way.

The total light transmittance of this extruded sheet was 85%, its haze value was 77, its 60-degree

specular gloss was 29, and its surface was uniform and extremely good.

Reference Example 3

The compounds that were used in Example 2 apart from allyl methacrylate were charged into a reaction vessel which was the same as that used in Example 1 (I), and an uncrosslinked polymer in the form of a powder was produced by the same procedure as in Example 1 (1).

The average particle diameter of the crosslinked polymer that was obtained in the form of beads was approximately 90 μ and its gel content was Q.

An extruded sheet was manufactured by the same procedure as in Example 1 (2) except that this uncrosslinked polymer which had been produced was used instead of the crosslinked polymer that was manufactured in Example 1 (1), and evaluations were made in the same way.

This molded sheet had a slightly ... (illegible) feel, the degree of its light diffusion was low, its 60-degree specular gloss, at 115, was high, and it was unsuitable for applications such as those of lighting covers, etc.

Reference Example 4

Compounds which were the same as in Example 2 except that 7 pts.wt. of allyl methacrylate was used were charged into a reaction vessel which was the same as that used in Example 1 (1), and a crosslinked polymer in granular form was produced by the same procedure as in Example 1 (1).

The average particle diameter of the crosslinked polymer that was obtained in the form of beads was approximately 90 µ, its gel content was 96 wt%, and its swelling degree was 29.

5

An extruded sheet was manufactured by the same procedure as in Example 1 (2) except that this crosslinked polymer which had been produced was used
10 instead of the crosslinked polymer that was manufactured in Example 1 (1), and evaluations were made in the same way.

This molded sheet had a rough and gritty surface,
15 an it was unsuitable for applications such as those of lighting covers, etc.

        Applicant for Patent : Mitsubishi Rayon KK
20   Agent   :   T. Yoshizawa, Patent
Attorney

Translation of Japanese Unexamined Patent Application 61-159440 A

LIGHT-SCATTERING ACRYLIC RESIN COMPOSITION

Publication No.   61-159440
Publication Date   19 July 1986
Inventor   Masao HAYASHI
Applicant   Asahi Chemical Industry Co., Ltd.
Int. Cl.⁴   C08L 33/12
Application No.   60-000150
Filing Date   7 January 1985

SPECIFICATION

1. Title of the Invention

Light-Scattering Acrylic Resin Composition

2. Claim

5   A light-scattering acrylic resin composition obtained by compounding 1–40 parts by weight of a crosslinked polymer to 100 parts by weight of a methyl methacrylate polymer, where said crosslinked polymer has a particle size of 30–300 μ and is obtained by polymerising 0.3–3 wt% of a crosslinking monomer with a non-crosslinking monomer consisting of:

10   10–90 wt% of an alkyl methacrylate in which the alkyl group has 1–4 carbons [1]*

     20–40 wt% of an aromatic vinyl monomer [2]

     5–50 wt% of an alkyl acrylate in which the alkyl group has 1–8 carbons.

3. Detailed Description of the Invention

Industrial field of utilisation

15   The present invention relates to a light-scattering acrylic resin composition having optical characteristics suited to light covers, etc., these optical characteristics being obtained by dispersing a light-scattering agent in an acrylic resin, thereby providing a high degree of both light scattering and light transmission.

Prior art

20   Light-scattering acrylic resins are valued and used as moulding materials for a variety of moulded products designed to give a feeling of refinement, and are particularly valuable as materials for light covers and signs.

Characteristics looked for in a light-scattering acrylic resin for use in application to light covers are a high degree of light scattering and, simultaneously combined with this, a high degree of light transmission. The latter characteristic is a quality that 25 is particularly desired from the point of view of efficient use of electrical energy.

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* Numbers in square brackets refer to Translator's Notes appended to the translation.

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To obtain a light-scattering resin it has been considered necessary to include an inorganic powder in the acrylic resin; and titanium oxide, barium sulphate, barium carbonate, calcium carbonate, silicon dioxide and calcium fluoride are among the substances which have hitherto been used in fine powdered form as this inorganic
5 powder.

Problem that the invention will solve

However, although resins to which these fine powders have been added exhibit a high degree of light scattering, they have also had the shortcoming that light transmission is low. For example, a problem encountered when such a resin is used
10 as a light cover is that if the light scattering is increased sufficiently for the light source not to show through the cover, the optical transmittance decreases and the light appears less bright.

Means for solving problem

The present invention has been devised with the object of solving the problem
15 described above. As a result of painstaking research, the present inventor has discovered a light-scattering agent that is capable of increasing the light-scattering performance without impairing the light-transmission performance. The present invention is the outcome of this discovery.

Namely, the light-scattering agent used in the present invention is a crosslinked
20 polymer of which the principal components are methyl methacrylate [3], an acrylic acid ester, and an aromatic vinyl monomer. The object of the invention is attained by mixing and dispersing this crosslinked polymer in an acrylic resin.

A resin of which the principal component is in particular methyl methacrylate is cited as the acrylic resin used in the present invention, and this will contain either a
25 methyl methacrylate homopolymer; or a copolymer consisting of methyl methacrylate and any one or more of methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, butyl acrylate, acrylonitrile, maleic anhydride, styrene or α-methylstyrene; or a mixture of a methyl methacrylate homopolymer and the above-described copolymer. With any of the above-mentioned possibilities, the proportion of methyl
30 methacrylate contained in the resin is preferably 50 wt% or more.

The crosslinked polymer which is the light-scattering agent in the present invention is a polymer with a particle size of 30–300 μ and is obtained by polymerising 0.3–3 parts [4] of a crosslinking monomer per 100 parts of a non-crosslinking monomer consisting of 10–90 wt% [5] of an alkyl methacrylate in which
35 the alkyl group has 1–4 carbons, 5–50 wt% of an alkyl acrylate in which the alkyl group has 1–8 carbons, and 20–40 wt% [6] of an aromatic vinyl monomer.

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1-40 parts by weight, and preferably 10-30 parts by weight, of the crosslinked polymer should be mixed to 100 parts by weight of the acrylic resin.

Methyl methacrylate, ethyl methacrylate, propyl methacrylate and butyl methacrylate are representative examples of the alkyl methacrylate with an alkyl group of 1-4 [7] that is used in the above-described crosslinked polymer. Ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc. are representative examples of the alkyl acrylate with an alkyl group of 1-8. [8] Styrene, vinyl toluene, α-methylstyrene, halogenated styrene, etc. can be used as the aromatic vinyl monomer. Allyl methacrylate, triallyl methacrylate, etc. can be used as the crosslinking monomer.

Effect of the invention

The light-scattering acrylic resin of the present invention is effective beyond all previous expectations and will be extremely useful industrially in respect of its high light scattering and high light transmission properties.

The terms "high light transmission" and "high light diffusion" [9] as used herein indicate a performance in which total light transmittance is 90% or greater and haze is 85% or greater.

Taking as an example application of a material as a light cover, if the total light transmittance is 90% or greater and haze is less than 85%, an image of the electric lamp under the cover is clearly visible, and hence a material with these properties cannot be used as a light cover. Hitherto well-known materials have been unable to cover the region where total light transmittance is 90% or greater and haze is 85% or greater. That is to say, with such materials, if haze is made 85% or greater, the total light transmittance ends up decreasing to less than 90% and so a light cover made from these materials will inevitably appear less bright. The present invention overcomes this defect of the prior art.

Embodiment 1

(1) Preparation of crosslinked polymer

The following compounds were placed in a reaction vessel provided with a stirrer and a condenser:

methyl methacrylate · · · · · · · 58 parts

styrene · · · · · · · · · · · · · · · · 25 parts

butyl acrylate · · · · · · · · · · · · · 16 parts

allyl methacrylate · · · · · · · · · · 1 part

n-octyl mercaptan · · · · · · · · · · 0.1 part

lauroyl peroxide · · · · · · · · · · · 2 parts

polyvinyl alcohol · · · · · · · · · · 2 parts

water · · · · · · · · · · · · · · · · · 250 parts

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Polymerisation was carried out at 80°C for 4 hours while stirring this mixture. After this, the temperature was raised to 90°C and held for 1 hour. After cooling, the product was dewatered and dried to give a polymer powder. The mean particle size of the obtained powder was 100 µ.

5   **(2) Preparation and evaluation of high light transmission, high light diffusion acrylic resin composition**

20 parts crosslinked polymer prepared in (1) above were added to 100 parts commercial acrylic resin powder (Delpowder 80N [10] manufactured by Asahi Chemical Industry), and after mixing in a Henschel mixer, the resin powder was

10   passed through an extruder and pelletised, and the resulting pellets injection moulded to form a 2 mm thick sheet. The total light transmittance of this sheet was 94% and its haze was 87%.

Embodiment 2

(1) Preparation of crosslinked polymer

15   In similar manner to Embodiment 1, the undernoted compounds were placed in a reaction vessel provided with a stirrer and a condenser and polymerisation carried out at 80°C for 3 hours under stirring. The temperature was then raised to 90°C and further polymerisation carried out for 3 hours. After this, the temperature was raised to 95°C and maintained for 1 hour.

20   After cooling, the product was dewatered and dried to give a polymer powder. The mean particle size of the obtained powder was 110 µ.

methyl methacrylate	33 parts
styrene	35 parts
butyl acrylate	30 parts
allyl methacrylate	2 parts
n-octyl mercaptan	0.1 part
lauroyl peroxide	2 parts
polyvinyl alcohol	2 parts
water	250 parts

30   **(2) Preparation and evaluation of high light transmission, high light diffusion acrylic resin composition**

30 parts crosslinked polymer prepared in (1) above were added to 100 parts commercial acrylic resin powder (Delpowder 80N manufactured by Asahi Chemical Industry), and after mixing in a Henschel mixer, the resin powder was passed through

35   an extruder and pelletised, and the resulting pellets injection moulded to form a 2 mm thick sheet. The total light transmittance of this sheet was 91% and its haze was 91%.

4

Asahi Chemical Industry

Comparisons 1-3

Table 1 outlines the composition and properties of the embodiments described above, together with those of comparisons in which an inorganic powder was used instead of the crosslinked polymer.

5

Table 1

	Acrylic resin	Crosslinked copolymer	Inorganic compound	Total light transmittance (%)	Haze (%)
Embodiment 1	100 parts Delpowder 80N	20 parts	—	94	87
Embodiment 2	100 parts Delpowder 80N	30 parts	—	91	91
Comparison 1	100 parts Delpowder 80N	—	1.5 parts $CaCO_3$	66	94
Comparison 2	100 parts Delpowder 80N	—	2 parts $BaSO_4$	62	94
Comparison 3	100 parts Delpowder 80N	—	5 parts CaF_2	73	93

Asahi Chemical Industry

AK/HMC/M12194

TRANSLATOR'S NOTES

1. In the amended claim, this range of 10–90 wt% is changed to 15–70 wt%.

2. In the amended claim, this range of 20–40 wt% is changed to 25–35 wt%.

3. Sic. However, according to the claim, this component is not specifically methyl methacrylate, but rather an alkyl methacrylate in which the alkyl group has 1–4 carbons.

4. Sic. However, the claim gives this amount of crosslinking monomer as 0.3–3 *wt%*.

5. This range of 10–90 wt% is changed in the Amendment to 15–70 wt%.

6. This range of 20–40 wt% is changed in the Amendment to 25–35 wt%.

7. Sic. By "the alkyl methacrylate with an alkyl group of 1–4", the writer presumably means "the alkyl methacrylate in which the alkyl group has 1–4 carbons".

8. Sic. Similarly, the phrase "the alkyl acrylate with an alkyl group of 1–8" is presumably an abbreviated way of saying "the alkyl acrylate in which the alkyl group has 1–8 carbons".

9. Sic. Previous to this point in the Japanese specification, the property provided in combination with a high degree of light transmission has been termed "(a high degree of) light scattering". Here, however, it is referred to as "light diffusion".

10. Sic. "Delpowder" seems to be a discontinued product name. However, according to the Asian Specialty Chemicals Newsletter, Issue 13, June 1999, Asahi Chemical Industry produced PMMA under its Plastic Chemical and Rubber Materials Division, under the trademark Delpet®.

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Translation of Amendment to JP 61-159440 A

- Amendment Filed in Accordance with the Provisions of
Section 17[bis] of the Japanese Patent Law, and published 15 April 1992

An amendment was filed, in accordance with the provisions of Section 17[bis] of the Japanese Patent Law, in respect of Patent Application No. 150 of 1985 (published 19 July 1986 under Publication No. 61-159440). The amendment is reproduced below.

AMENDMENT (Published 15 April 1992)

Date of filing of amendment: 20 December 1991

To: Director-General of the Patent Office

1. Case Identification

Patent Application No. 150 of 1985

2. Title of the Invention

Light-Scattering Acrylic Resin Composition

3. Person Filing Amendment

Relation to Case: Applicant: Asahi Chemical Industry Co., Ltd.

4. Parts Amended

The sections "Claim" and "Detailed Description of the Invention" of the specification.

5. Substance of the Amendment

The specification is amended as follows.

(1) The claim is amended as follows:

Claim

A light-scattering acrylic resin composition obtained by compounding 1–40 parts by weight of a crosslinked polymer to 100 parts by weight of a methyl methacrylate polymer, where said crosslinked polymer has a particle size of 30–300 μ and is obtained by polymerising 0.3–3 wt% of a crosslinking monomer with a non-crosslinking monomer consisting of:

15–70 wt% of an alkyl methacrylate in which the alkyl group has 1–4 carbons

25–35 wt% of an aromatic vinyl monomer

5–50 wt% of an alkyl acrylate in which the alkyl group has 1–8 carbons. [1]*

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* Numbers in square brackets refer to Translator's Notes appended to the translation.

(2) "10–90" in line 14 of page 4 is amended to "15–70". [2]

(3) "20–40" in line 16 of page 4 is amended to "25–35". [3]

(4) The following is inserted between line 19 and line 20 of page 4: [4]

"An increase in the aromatic vinyl monomer, which is a non-crosslinking monomer, has the following effect on the characteristics of the light-scattering acrylic resin: namely, there is a tendency for haze to increase and for the total light transmittance to decrease. That is to say, if the aromatic vinyl monomer exceeds 35 wt%, haze is 85% or greater, but the total light transmittance becomes less than 90%. If the aromatic vinyl monomer is less than 25 wt%, the total light transmittance is 90% or greater, but haze becomes less than 85%. Consequently, in order to make haze 85% or greater and total light transmittance 90% or greater, the aromatic vinyl monomer has to be 25–35 wt%."

(5) The following is inserted between line 6 and line 7 of page 9: [5]

"Embodiments 3 and 4
Other than using the crosslinked polymer compositions shown in Table 1, approximately the same operations as in Embodiment 1 were carried out. The results are shown in Table 1."

(6) The following is added after line 9 of page 9: [6]

"Comparisons 4–7
Other than using the crosslinked polymer compositions shown in Table 1, approximately the same operations as in Embodiment 1 were carried out. The results are shown in Table 1."

(7) Table 1 on page 10 is amended to Table 1 given on the accompanying sheet.

Table 1

	Acrylic resin	Crosslinked copolymer		Crosslinked copolymer composition				Inorganic compound	Diffusion sheet		
		Loading (parts)	Particle size (μ)	Methyl methacrylate (wt%)	Styrene (wt%)	Butyl acrylate (wt%)	Allyl methacrylate (wt%)		Sheet thickness (mm)	Total light transmittance (%)	Haze (%)
Embodiments 1	100 parts Delpowder 80N	20	100	58	25	16	1	—	2	94	87
2	"	30	110	33	35	30	2	—	"	91	91
3	"	3	30	56	25	16	3	—	"	94	87
4	"	8	50	45	30	22	3	—	"	92	89
Comparisons 1	"	—	—	—	—	—	—	1.5 parts $CaCO_2$	"	66	94
2	"	—	—	—	—	—	—	2 parts $BaSO_4$	"	62	94
3	"	—	—	—	—	—	—	5 parts CaF_2	"	73	93
4	"	3	30	40	40	17	3	—	"	89	92
5	"	8	50	43	45	10	2	—	"	87	93
6	"	20	100	40	20	38	2	—	"	94	84
7	"	15	80	58	15	26	1	—	"	94	82

TRANSLATOR'S NOTES

1. I reproduce the underlining that is used in the Japanese amendment to indicate which part or parts of the original text have been changed in the amended version.

2. This corresponds to line 34 of page 2 of the translation of the Japanese specification.

3. This corresponds to line 36 of page 2 of the translation of the Japanese specification.

4. The corresponding insertion position in the translation is before the paragraph beginning on line 1 of page 3.

5. The corresponding insertion position in the translation is before the section beginning on line 1 of page 5.

6. The corresponding insertion position in the translation is after line 4 on page 5.

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(54) Tinted acrylic resin sheets

(57) Tinted acrylic resins, most preferably sheets, with zones of different colour on one surface are produced by bulk polymerisation of a matrix polymer precursor which is homogeneously tinted in the presence of a ground, also tinted, acrylic resin which differs in colour from the matrix polymer. The tinted acrylic resin settles in the base region of the chamber, and when finally the polymerised object is removed from the mould, zones of different colour are present on the underside giving the overall impression of a "stone structure". The coloured structure is retained even after tempering and moulding, for example, in the formation of sanitary ware.

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Tinted Acrylic Resins

5   The invention relates to tinted acrylic resins, in
particular a process for the preparation thereof. More
particularly it relates to a process for producing
coloured polyacrylate articles such as sheets,
particularly polyalkylmethacrylate sheets having zones
10 of different colours on a surface thereof.

There are available in the art colouring agents for
tinting synthetic resins in almost any desired manner.
In many cases, it is, however, desirable to tint the
visible surface of the synthetic resin in different
15 colours. The aim may be to produce plastic surfaces
with randomly incorporated "islands" which differ from
the basic resin by a particular colour or brightness, or
to produce coloured patterns of a predetermined geometry
20 on the surface of the plastic. In certain fields of
application, e.g. in the sanitary ware sector, it was
well known to produce ceramic materials with differently
coloured tints, which were frequently known by the term
"rustic decor".

25
DE-PS-693 824 proposes a process for embedding dyestuff-
containing layers in moulded polymers obtained from
liquid polymerisable organic compounds. In this process
dyestuff-containing layers which contain a binder
30 insoluble in the compounds to be polymerised, are
applied to the wall of the polymerisation mould and
after the compound to be polymerised has been poured in,
polymerisation is carried out in known manner. DE-A-30
23 964 proposes a process for producing dyestuff-
35 containing zones in acrylic and methylacrylic resins
near the surface thereof in the course of the polymer-
isation of the monomers and pre-polymers forming the

resins in the polymerisation chambers which shape the objects. In this process, first a dyestuff homogeneously distributed in a binder is applied as a coating to the wall of the shaping polymerisation chamber, the binder

5 being soluble or at least swellable in the liquid resin or in its precursors. After the monomers and/or prepolymers which are to be polymerised have been introduced, polymerisation is carried out in a manner known per se.

10

EP-A-2 108 discloses tinted acrylic sheets which contain an unevenly distributed inorganic pigment and an evenly distributed dyestuff. The particles of the unevenly distributed pigments are concentrated predominantly on

15 one surface of the sheet, whilst the opposite surface, which is preferably substantially free from pigment, is still visible. This produces a 3-dimensional impression of depth in the tinting of acrylic glass.

20 EP-B-60935 relates to a process for producing objects from plastics based on acrylic and/or methacrylic resin, the surface of which has zones of different colours. In the course of conventional chamber polymerisation, dyestuff- containing bead polymers are added to the

25 acrylate or methacrylate monomers and prepolymers contained in the chamber, then polymerisation of the monomers is carried out and finally they are removed from the mould. The acrylic or methacrylic resin may also contain dyestuff. The sheets produced by this

30 method can also be deformed in conventional manner. The teaching of EP-B-60935 results in interesting products which thoroughly satisfy the expectations of the art with regard to this type of object. However, the requirements with regard to pattern and structure of the

35 objects (which means mainly their surfaces) are many and varied, which means that one cannot expect to satisfy all the requirements using a single technical method.

Traditionally, people have surrounded themselves with
ceramics and stone as materials in varying forms and
decorated in different ways. The development of
5   plastics has further increased the possibilities with
regard to material properties and appearance. Thus, in
the early days, plastics such as acrylic resins with a
superficial marble appearance were produced. Synthetic
resins have also acquired considerable importance as
10   binders for mineral materials in synthetic stone,
polymer concrete and the like. The existing range of
possibilities appeared to be in need of expansion,
particularly in the direction of surfaces emphasising a
mineral, stone-like impression. It has now been found
15   that the acrylic resin articles, preferably sheets
produced by the process according to the present
invention have surfaces which come very close to these
guiding principles.

20   In one aspect the present invention therefore provides
a method for producing a tinted acrylic resin sheet
having zones of different colour on one surface thereof,
said method comprising
     a)   homogeneously tinting the precursor of a matrix
25   polymer;
     b)   distributing in the matrix polymer precursor a
           ground, acrylic resin tinted with a colour
           different to that of the matrix polymer;
     c)   effecting polymerisation of the matrix polymer
30   containing the acrylic resin in a polymerisation
           vessel, whereby the acrylic resin is deposited in
           the base region of the vessel.
     The polymerization is preferably radical
polymerization.
35   Generally, the content of ground, tinted acrylic
resin in the tinted acrylic resin sheets according to
the invention is conveniently from 1 to 20% by weight,

preferably 2 to 10%, more preferably 2 to 5% by weight.

The procedure according to the invention might initially
appear to be a backward step when compared with the
prior art, including as it does a more complicated
method of producing the acrylic resin which is to be
added in order to bring about the differentiation of
colour in the end product. The grinding process in
particular requires equipment which is satisfactory from
the point of view of operational hygiene and safety
(because of the risk of dust explosions). (See H.
Rumpf, Kunststoffe 44, page 43, 93, (1954)). However,
irrespective of this, the process according to the
present invention nevertheless results in polyacrylate
sheets which unexpectedly meet the requirements of the
art for plastics with a stone-like appearance to a high
degree.

Suitable precursors of the matrix material or matrix
polymer for the tinted acrylic resin sheets prepared
according to the invention include the known prepolymers
and syrups based on acrylic resin and the acrylate or
methacrylate monomers and mixtures which contain the
monomers. They may be synthesised predominantly from
esters of acrylic or methacrylic acid, particularly
methylmethacrylate as monomer. In addition, other co-
polymerised monomers such as styrene and the alkylated
derivatives thereof, such as α- and p- methylstyrene,
vinylesters of carboxylic acids such as vinylacetate,
amides of acrylic or methacrylic acid or acrylonitrile
may be co-polymerised, usually in amounts of less than
50% by weight, e.g. from 0 to 40% by weight, for example
5 to 30% by weight, based on the total monomer content.
(see Ullmanns Encylopädie der Techn. Chemie, 3rd
edition, volume 14, pages 109 and 110, Urban and
Schwarzenberg).

Examples of suitable esters include, apart from methyl-
methacrylate (MMA), the methyl ester of acrylic acid,
the ethyl, butyl, 2-ethylhexyl, cyclohexyl and phenyl
esters of acrylic and methacrylic acid. Other suitable
5   compounds include amides such as acrylamide or
methacrylamide, N-methylolacrylamide and -
methacrylamide, and optionally also the acids or salts
of acrylic and methacrylic acid.

10   The content of MMA in the matrix polymers is preferably
more than 50% by weight, more preferably more than 80%
by weight, especially more than 90% by weight and upto
substantially 100% by weight, based on the total monomer
content. The choice of monomers will depend on the
15   fields of application and the requirement profiles of
the plastics in question. Primarily, the material will
be used for moulded objects in the fields of
engineering, sanitary ware and household items. These
require, _inter alia_, plastics which are distinguished by
20. being insoluble in conventional solvents as well as
having favourable mechanical properties; possibly a high
impact strength. As a guide, a VICAT value for the
matrix polymer (according to DIN 53 460) of more than
100°C would be required.

25

Cross-linking monomers such as ethylene glycol dimethyl
acrylate, 1,4-butanedioldimethacrylate, triglycoldi-
methacrylate, trimethylolpropanetrimethacrylate or allyl
compounds, such as allylmethacrylate, triallylcyanurate
30   or triallylisocyanurate may conveniently be present.

The polymerisation may be carried out in a manner known
per se using the experiences of the art (see H. Rauch-
Puntigam and Th. Völker in "acryl- und Methacryl-
35   verbindungen", Springer-Verlag 1967 and J. Brandrup -
E.H. Immergut, Polymer Handbook, 2nd Edition, Wiley-
Interscience (1975)). Similar techniques have already

been described in outline in German patent No. 639 095.
The initiators for polymerising polymerisable double
bonds such as those in acrylic monomers, styrene and
derivatives thereof, esters of vinyl compounds, may
include for example peroxide or azo compounds in the
conventional quantities. The molecular weight may be
controlled by means of the known regulators in the
concentrations known per se. Organic sulphur compounds
are, for example, suitable regulators. The degree of
polymerisation and hence the molecular weight of the
resin molecules produced can be adjusted, as is well
known, by means of the concentration of initiator and/or
regulator. Thus, during the polymerisation of acrylic
resins, 0.01 to 1.0% by weight of initiator will
conveniently be used. The quantity of regulator added
is conveniently between 0.01 and 0.5% by weight,
preferably between 0.05 and 0.2% by weight. In general,
the molecular weights (Mw) of the matrix polymers are in
the range from $2 \cdot 10^5$ to $5 \cdot 10^6$.

In the majority of cases the matrix polymer is weakly
cross-linked, the Vicat softening temperature (according
to DIN 53 460, method B) is generally above 100°C. The
polymerisation mixtures may also contain adjuvants known
per se, such as UV-absorbers, plasticisers, thermo-
stabilisers, antioxidants, flame retardants, etc.

The preferred method of polymerisation is bulk polymer-
isation, particularly by the chamber method. (see Th.
Völker, H. Rauch-Puntigam", Acryl- und Methacryl-
verbindungen", Springer-Verlag, 1967). With a typical
mixture, for example, the starting materials may be a
syrupy poly-methylmethacrylate (PMMA) prepolymer with a
conversion of about 20% and an average molecular weight
of 250,000 g/Mol. Advantageously, the matrix polymer is
tinted by the addition of one or more suitable colouring
pigment pastes to the prepolymer mixture, preferably

with mechanical distribution by stirring. (For the production of the pigment pastes see below). Generally, the dyestuff content of the matrix polymer will not exceed 2% by weight; in the majority of cases it should

5   range from 0.3 to 0.8% by weight. The prepolymer mixture, for example the above-mentioned syrupy PMMA prepolymer, expediently already contains the radical initiator, such as azo-isobutyronitrile (about 0.8 parts by weight) and preferably the cross-linker, for example

10 triallylcyanurate in quantities of about 5 parts by weight to 1000 parts by weight of prepolymer.

Basically, the technology described above for producing the matrix polymer can also be used to produce the

15 tinted acrylic resin which is subsequently ground. Similarly, the same starting compounds such as monomers and prepolymers may be used as starting materials, but there are certain limits with regard to the particular composition, without having a clearly negative effect on

20 the mechanical properties of the end products.

In contrast to the matrix polymer in which (weak) cross-linking may be advantageous, the tinted acrylic resin is generally not cross-linked. The tinting of the acrylic

25 resin is also advantageously carried out using colouring pigment pastes which are introduced into the polymerisation mixture for the acrylic resin with mechanical distribution, preferably with stirring, and are usually homogeneously distributed. The dye-stuffs

30 or pigments suitable for colouring are known (see Vieweg-Esser, Kunststoff-Handbuch, Vol. IX, "Polymethacrylate" Carl Hanser Verlag, 1975; H. Batzer, "Polymere Werkstoffe", Vol. II, Technologie 1, page 337-353, Georg Thieme Verlag, 1984).

35

Once again, the polymerisation is conveniently carried out by the bulk polymerisation method of the prior art.

Expediently, polymerisation may be carried out in a suitable vessel, e.g. by the chamber method. As a guide, a temperature of about 45°C (e.g. when azo-isobutyronitrile is used as initiator) and a duration of about 15 hours are required. Conveniently, temperature adjustment is subsequently carried out, for example at about 115 ± 5°C in a circulating air cupboard.

The articles, e.g. sheets obtained are comminuted, more particularly ground to the required degree of fineness of the ground material in a manner known per se (see H. Rumpf, loc.cit, H. Batzer "Polymere Werkstoffe", Vol. II, Technologie 1, 105-111 Georg Thieme Verlag, 1984). The particle size and particle size distribution will expediently depend on the intended use. In general, the particle size range (diameter) which is of interest within the scope of the present invention is between 0 and about 5 mm, preferably 0.001 to about 5 mm, more preferably 0.01 to about 3 ± 1 mm, whilst the smaller particles (smaller than 0.1 mm) may possibly contribute less to the overall impression of "stone structure" than to the overall impression of colour. A particle fraction larger than 0-1.0 mm will give a significantly finer "stone structure" than a fraction ranging from less than 0.1 mm to 3.0 mm. Grinding with a cross beater mill for example, has proved satisfactory. The particle fractions can be separated in the usual way, for example by screening (see Kirk-Othmer, Encyclopaedia of Chemical Technology 3rd edition, Vol. 21, page 114 J. Wiley 1983.) Generally, the proportion of ground tinted acrylic resin in the coloured acrylic resin sheets, i.e. the finished product, is from 1 to 20% by weight. The acrylic resins may usefully be incorporated and distributed in the matrix polymer by stirring, for example using a stirring mechanism at a speed of 300-1000 rpm.

The preparation and use of the colouring pigment pastes is known _per se_ and constitutes a preferred method of colouring polymers (see H. Balzer "Polymere Werkstoffe" loc.cit, page 349). The dyestuff, more particularly the pigment or pigments together with the polymer, here preferably PMMA and the monomer, preferably methylmethacrylate, is triturated with the aid of a fast-operating disperser. The content of dyestuff is conveniently in the range of 10 to 70% by weight, preferably between 25 and 50% by weight.

When tinting to give an overall impression of "stone structure", black pigments and white pigments will naturally play a decisive part.

The white pigments used are advantageously titanium dioxide, zinc sulphide (Sachtolith) with a blueish white colour, the mixed pigment Lithopone [R] and in addition antimony trioxide, as well as calcium carbonate and sulphate, barium sulphate, talc, kaolin and the like. The black pigments used are predominantly carbon black, whilst in the case of objects which will come into contact with food, a maximum 0.15% by weight of fractions which are capable of being extracted with toluene may be present.

Yellow or red colouring is safely achieved by the use of suitable iron oxide pigment, whilst blue or green tones may be produced using ultramarine pigments and cobalt pigments.

Acrylic resin articles, e.g. sheets can be produced according to the invention which have zones of different colours on the (original) underside, lending a stone-like appearance. In the embodiment described by way of example, a surface is thus obtained with a plurality of

small black and white flecks with jagged contours on a
brown background colour, for example. The coloured
structure is retained even after tempering and moulding
to form an item of sanitary wear. By a suitable choice
5   of particle size and nature of the colouring, the
character of "stone structure" can be adjusted between
very fine and rather coarser and the shade of colour can
be adjusted from predominantly white to coloured or
black.

10

The examples which follow serve to illustrate the
invention in a non-limiting manner. The "parts"
specified are parts by weight. The molecular weight can
be determined using gel permeation chromatography.

EXAMPLES

A)   PRODUCTION OF PIGMENTED GROUND PMMA PARTICLES FOR
      COLOURING ACRYLIC GLASS WITH A STONE-LIKE DECOR.

Example 1

0.8 parts of 2,2'-azobis-(isobutyronitrile) are stirred
into 1000 parts of a syrupy PMMA prepolymer with a
conversion of 20% and an average molecular weight MW of
250,000 g/Mol.   From a mixture of 15 parts of a white
pigment and 4 parts of a soluble PMMA resin, a pigment
paste is triturated using known methods with 40 parts of
methylmethacrylate and using a fast-operating disperser
and the pigment paste is added to the above mixture with
stirring.   The mixture is transferred into a chamber
measuring 40 by 50 cm and 4 mm thick.   Polymerisation is
carried out for 15 hours at 45°C and subsequently the
polymer is adjusted to a temperature of 115°C in a
circulating air cupboard.   The white PMMA sheet obtained
is then ground up in a cross beater mill.   The particle
distribution ranges from less than 0.1 mm to about 3.0
mm.   If necessary, individual factions may be screened
off.

Example 2

The same procedure as example 1 is adopted except that
the pigment paste is triturated with 0.2 % of a black
pigment.   A black ground powder is obtained.

B)   METHOD OF PRODUCING COLOURED, PATTERNED ACRYLIC
      GLASS FOR USE IN SANITARY WARE.

Example 3

0.8 parts of 2,2'-azobis-(isobutyronitrile) and 5 parts

of triallylcyanurate are stirred into 1000 parts of a
syrupy PMMA prepolymer with a conversion of 20% and an
average molecular weight MW of 250,000 g/Mol.   From a
mixture of 5 parts of a white pigment and 5 parts of a
brown pigment and 0.3 parts of a black pigment, the
pigment paste is triturated using known methods with 4
parts of a soluble PMMA resin and 40 parts of methyl-
methacrate using a fast-operating disperser and the
pigment paste is added to the above mixture with
stirring.   20 parts of the ground white substance from
Example 1 and 20 parts of the ground black substance
from Example 2 are added to this basic mixture, stirring
is continued for about 15 minutes and this mixture is
transferred into a chamber measuring 40 by 50 cm and 4
mm thick.   Polymerisation is carried out at 45°C for 15
hours and the chamber is then adjusted to a temperature
of 115°C for 5 hours in a circulating air cupboard.   A
PMMA plate is obtained which, on its underside, has a
uniform distribution of small black and white jagged
points on a brown background.   After temperature
adjustment and moulding into an article of sanitary
ware, the coloured structure is retained.

Example 4

The same procedure as Example 3 is adopted, except that
the pigment paste is obtained from a mixture of 2.5
parts of a brown pigment and 2.5 parts of a black
pigment. The ground particles consist of 20 parts from
Example 1 (the screened particle fraction from more than
0 to 1.0 mm) and 20 parts from Example 2 (the screened
particle fraction from > 0 to 1.0 mm).   A dark-brown
PMMA is obtained which on its underside has a uniform
distribution of black and white irregular points and
jagged dots.   The structure is considerably finer than
that of Example 3.

Example 5

The same procedure as Example 3 is adopted, except that
the pigment paste is obtained from a mixture of 10 parts
5   of a white pigment, 0.1 parts of a brown pigment and 0.1
parts of a black pigment. The mixture, analogously to
Example 4, is added as ground material. A PMMA sheet is
obtained which has on its underside a uniform
distribution of black and white irregular jagged dots on
10   a grey background.

14

Claims:

1.   A method for producing a tinted acrylic resin
article such as a sheet having zones of different colour
5   on one surface thereof, said method comprising
    a)   homogeneously tinting the precursor of a matrix
        polymer;
    b)   distributing in the matrix polymer precursor a
        ground, acrylic resin tinted with a colour
10   different to that of the matrix polymer;
    c)   effecting polymerisation of the matrix polymer
        containing the acrylic resin in a polymerisation
        vessel, whereby the acrylic resin is deposited in
        the base region of the vessel, and
15   d)   removing the final article from the mould.

2.   A method as claimed in claim 1 wherein said
polymerization is bulk polymerization.

20   3.   A method as claimed in claim 1 or claim 2 wherein
said polymerization is effected in a shaping
polymerization chamber.

4.   A method as claimed in claim 3 wherein the acrylic
25   resin settles in the base region of said chamber, and a
sheet product is removed from the mould.

5.   A method as claimed in any of the preceding claims
wherein the acrylic resin has a particle size in the
30   range 0.001 to about 5 mm in diameter.

6.   A method substantially as herein described with
reference to the Examples.

35   7.   A tinted acrylic resin sheet when prepared by a
method as claimed in any of the preceding claims.